CHAPTER – I

INTRODUCTION
AND
LITERATURE REVIEW

INTRODUCTION :

Glass is considered as one of the most principle and important materials . It plays an important role in our life for its great contribution in scientific research and industry .

The history of glass is a very old one , that of its scientific understanding is very new , however , during the last three decades , many efforts have been made in order to investigate and identify types of glasses from the scientific point of view .

Without a through knowledge of the relationship between the structure and glass properties , no important progress is any longer possible . This has been recognized and the modern glass research establishment is being set up all over the world .

I-1 : Glass Definition :

There are several attempts to give a technological definition to the term glass . The most acceptable definition of this term has been stated by Rawson(1) (1967), that a glass is being the product of fusion of some materials which have been cooled to a rigid condition without crystallization i.e. , the glass is considered as a material which can be obtained by cooling from the normal liquid state without any discontinuous change in its properties at any temperature, but it has become more or less rigid through a continuous change in its viscosity .

The word glass or vitreous substance is usually used to refer to a lustrous and transparent material . However , it becomes clear after words that these properties are not sufficient to describe " Glass ".

A number of glass types , in particular the metallic and chalcogenides glasses , are opaque in the visible region of spectrum .

The American Society for Testing Materials (ASTM) defined glass as "an inorganic product of fusion which has been cooled to a rigid condition without crystallization " . This definition is too restrictive as many organic glass systems are known and fusion is not the only means of making a glass .

In Fig (1-1) the changes in specific volume (volume per unit mass) that would occur as a simple , imaginary substance is cooled from the liquid state so as to from, (a) a crystalline solid and (b) a glass . When the liquid is cooled very slowly an abrupt change occurs in the specific volume and in other physical properties at a characteristic temperature , the melting point of a substance , where the material crystallizes . When the liquid is cooled rapidly there is no abrupt change in specific volume at any temperature , instead the slope of the specific volume temperature curve changes continuously over a range of temperature . At low temperature, the rate of change of volume with temperature is similar for both the glass and crystalline material , but the absolute magnitude of the specific volume of the glass is much larger and it also varies with the rate at which the original liquid was cooled .

The transition from the liquid to the glassy state takes place over a range of temperature , there is no clearly defined transition temperature which could be compared with the melting point of a crystalline solid(2) .

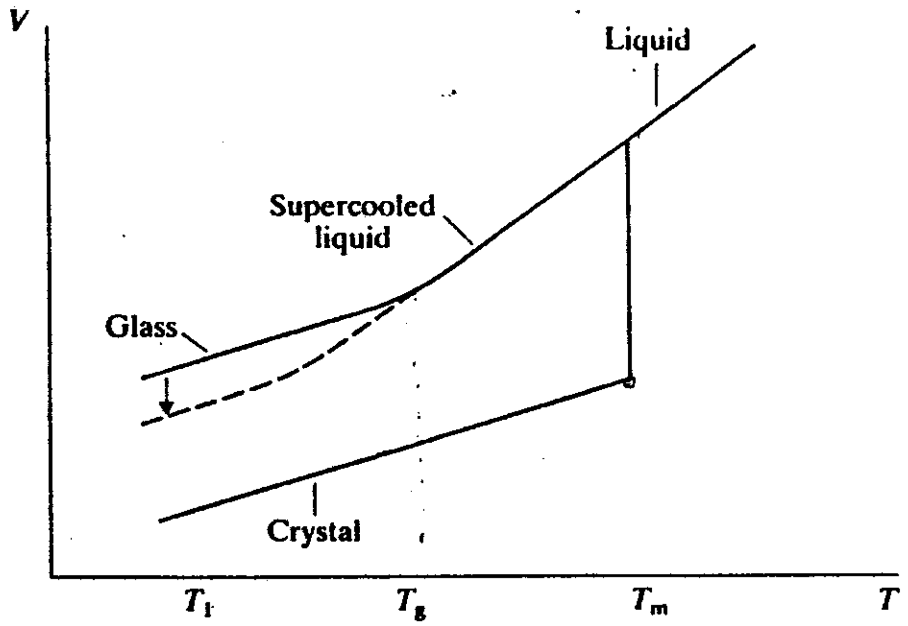

Fig. (I–1): Schematic of a volume –temperature dependence for the material in various states.

I-1-1 : The Structure of Glass :

Glasses , like ordinary liquids , posses only short – range order, and from their X-ray diffraction patterns it is known that , both glasses and liquids have the same structure . On the other hand as the temperature is lowered, the degree of order in a liquid increases whereas in glass it does not approach the crystalline state as the temperature is lowered .

First real advance in the theory of the glass structure is due to Zachariasen(3) who proposed the random network theory i.e. a structural lacking symmetry and periodicity in contrast with the crystalline structure .

I-1-2 : The Random Network Theory :

Zachariasen(3) began with the idea that the atoms in glass must be linked by forces essentially the same as in crystals , as well as they oscillate about a definite equilibrium position , this was deduced from the fact that the strength of the glass is of the same order as the strength of the crystal . As also in crystals the atoms in glass must form an extended three - dimensional network , but not periodic , this was shown by the absence of sharp X-ray diffraction spectra . Zachariasen then proposed the following condition for glass formation : of $Si\,O_4$ and $Al_2\,O_3$ glasses , Fig (1-2) :

1) Each oxygen ion is linked to no more than two cations.
2) The oxygen polyhedran share corners with each other not edges or faces .

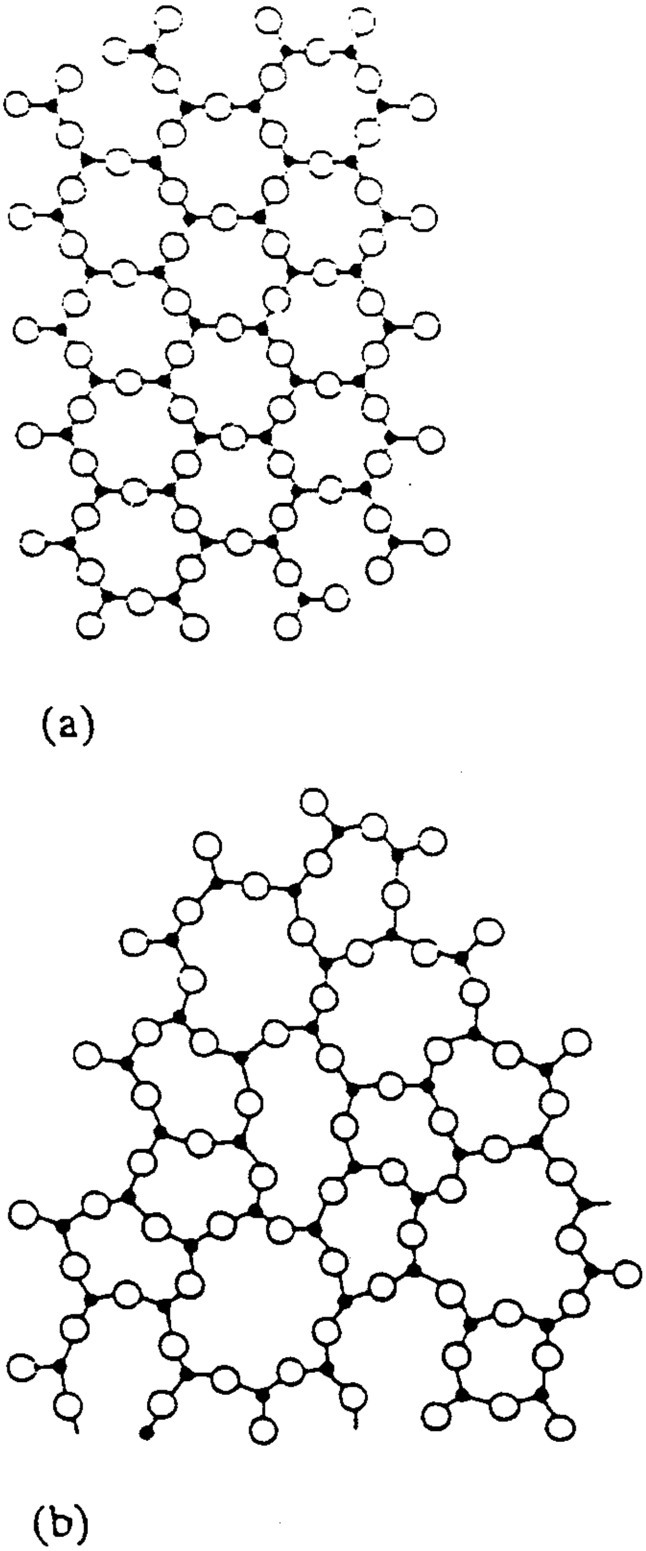

Fig.(1–2):Schematic two –dimensional representation of the structure of
(a) ahypothetical crystalline compound Al_2O_3 and
(b) the Zachariasen model for the glassy form of the same compound

3) The number of oxygen atoms surrounding the positive ion must be small (3 or 4) .

4) At least three corners of each oxygen polyhedron must be shared with another polyhedron .

The oxides A_2O_3 can do so if the oxygens form triangles around each A atom and for the oxides AO_2 and A_2O_5 can do so if the oxygens form tetrahedra around each A atom . It was considered probable that condition (2) ruled out the oxides AO_3 , A_2O_7 and AO_4 .

I-1-3 : Glass Formation :

Glass formation is not a rare phenomenon , many materials form glasses in relatively large masses (greater than 1 gm) and at moderate cooling (greater than 1 C/min) .

According to the free volume model of the liquid state developed by Cohen and Turmbull(4) , all liquids would undergo a glass transition to an amorphous solid except for those liquids which usually form crystalline solids . Thus , according to this point , glass formation prevents crystallization , and the explanation of why certain materials are good glass formers than other was trended in detail by Turnbull and Cohen(5,6), so they have stated that glass formation becomes more probable , the greater the cooling rate , the smaller the sample and the slower the crystallization rate .

It was found also that all crystalline oxides which are suited to form a glass satisfy the condition of Zachariasen and reversibly each oxide satisfying conditions can appear in the vitreous state . These oxides are usually classified as oxide glass formers . Many empirical sequences are usually applied in order to obtain such classification, but neither of them are absolutely succeeded. They usually failed at certain special abnormal condition. However in the following each group of oxides will be defined:

i) Glass Formers:

Silicon (SiO_4) Boron oxide (B_2O_3), phosphorous penta oxide (P_2O_5) , Germanium oxide (GO_2)and Arsenic oxide (As_2O_5) are good examples of this group. Applying Zachariasen requirement it can be seen that their cations are small , highly charged and their coordination number are usually small. Accordingly all of them are suited for glass formation and hence they usually called glass formers.

ii) Modifiers:

Oxides , like Na_2O_3 , K_2O_3 , CaO , BaO, ect .. are usually added to the glass formers oxides in order to modify the prepared glasses . Their cations like, Na^+, K^+, Ca^{++}, Ba^{++} are of large size and of small charge , so, they find their places in the interstices of the network consisting of the oxygen polyhedra. They also have only a small effect on the internal energy of the network.

iii) Intermediate:

Dietzel (7) showed that there are a number of oxides which have an intermediate position between network formers and network modifiers , this means that they play the role of both. Examples of these ions are Be^{++} , Zn^{++}, Pb^{++}, Fe^{++}, Co^{2+} , Ni^{2+} and Ti^{4+}. They appear to be capable of replacing the formers in the network structure up to a higher content , But they also can not form glasses when melted alone .

Generally speaking a glass can be formed when one or more , a glass - forming oxides are mixed , with or without one or modifying oxides or oxides intermediate type .

I-2 : Band models :

This present section is a review of the phenomena of electrical conduction in amorphous semi-conductors . An attempt will be made to unify the discussion around Anderson's electronic transport and the electronic band structure of vitreous semiconductors and insulators .

Several models were proposed for the band structure of amorphous semiconductors , which have the same extent that they all used the band tails . Opinions vary , however as to the extent of this tailing .

I-2-1 : The Simplest Band Model :

Economou(8) and others presented a band structure model for the amorphous semiconductors , as shown in Fig(I-3) . They suggested that the band structure consist of localized states (dashed area) above E_v and a conduction band (C.B.) with a tail of localized stares below E_c . They proposed that the states from E_v to E_c are localized and extended outside it .

Anderson(9) proposed that the electrons in the localized states can not diffuse at zero Kelvin , but at a definite temperature they presumably can contribute to the conductivity by assisted hopping only .

The localized states can be found , according to Mott(10) , when a dangling bond is formed , then a filled state is pulled out from the valence band and an unoccupied state is formed in the conduction band . These produce localized states in the forbidden gap , a donor

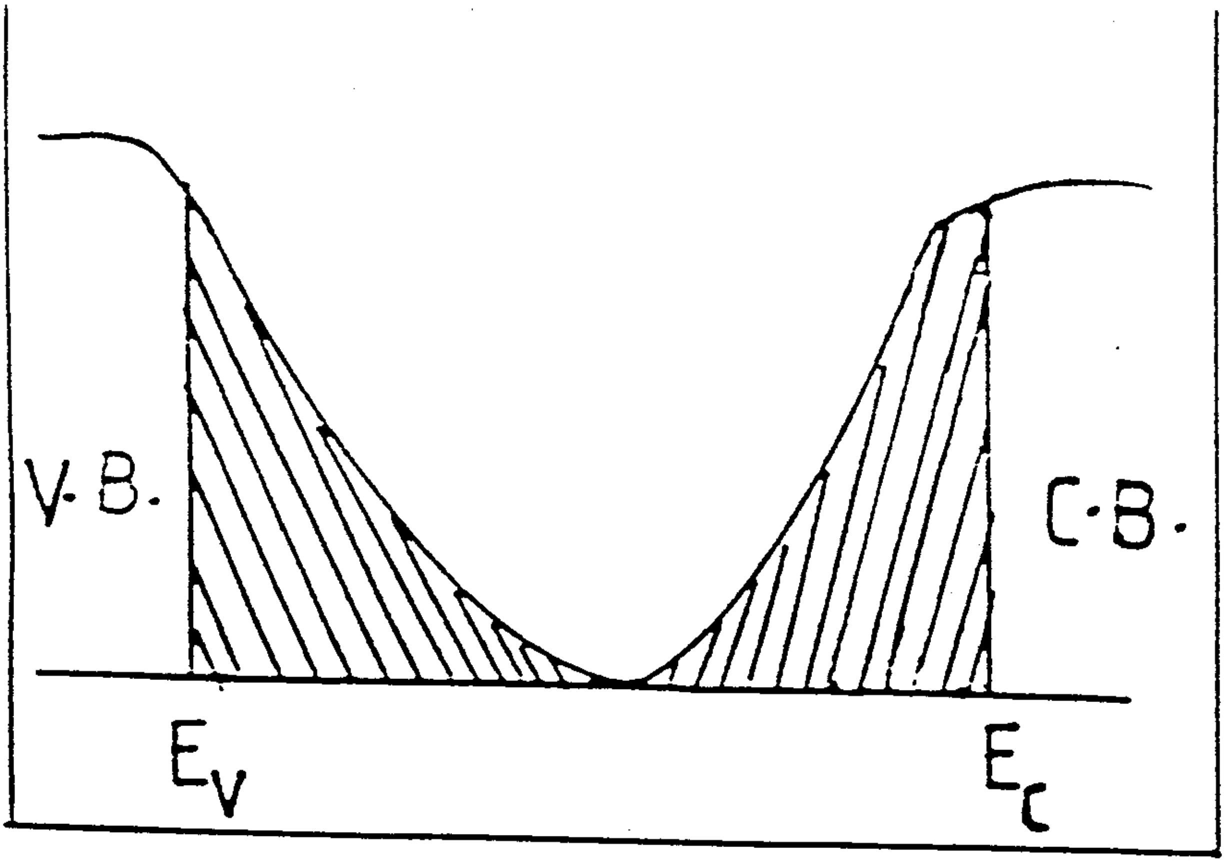

Fig.(I–3): The simplest model for amporphous semiconductors.

near the gap center and above it acceptor one exists only when the donor is occupied .

I-2-2 : Mott – CFO Model :

Mott$^{(11,12)}$ and Cohen et al$^{(13)}$ have developed a model for the electronic structure of amorphous semiconductor , this has come to be known as (CFO) model , as shown in Fig. (1-4) , this model is derived from the concept of the ideal covalent random network structure , simple chemical considerations and some physical observations suggest that the valence and conduction bands are separated by a gap Transitional and compositional disorder are assumed to cause fluctuation of the potential of sufficient magnitude that they give rise to localized states extending from the conduction and valence bands into the gap . These localized states are not associated with definite imperfaction but are the result of the randomness of potential barrier their number and energy depend on the degree of randomness and strength of scattering it is important to the valence band tail not that the states are assumed to neutral when occupied and the conduction band tail states are neutral , when empty. This places the Fermi energy some where near the gap center.

The character of the wave function changes at critical energies E_c and E_v which separate the extended and localized states .

Here electron and hole mobilities drop sharply from a low mobility band transport with finite mobility at T = 0 °K to a-thermally activated hopping between localized gap states which disappear at T = 0 K .

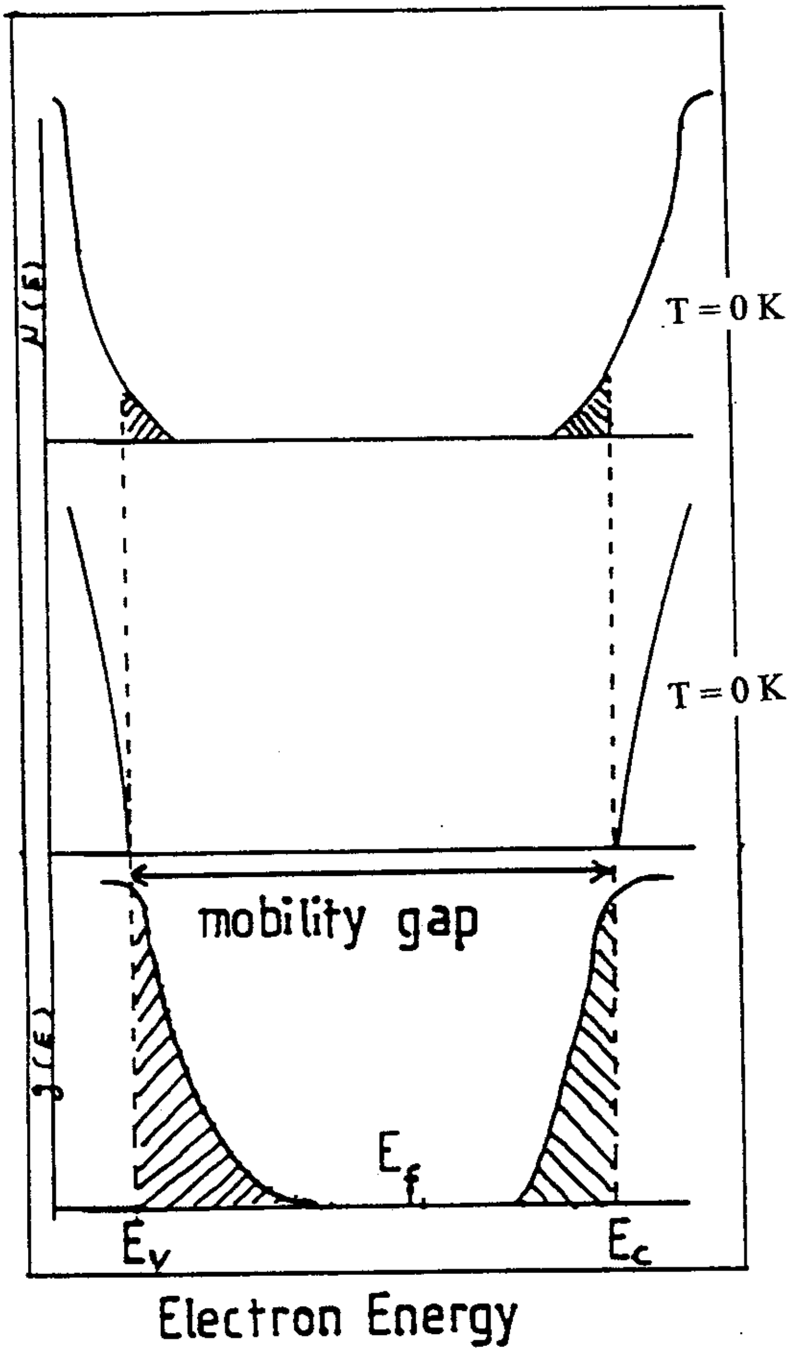

Fig. (I-4) :

Sketch of Mott-CFO model for covalent semiconductors. The distribution of localized states may be non monotonic when defect states of a certain energy are prevalent.

The so called mobility edges , define a mobility gap ($E_c - E_v$) which contains only localized states , this model is believed to be applied to alloy glasses which contain compositional as well as positional disorder . It was originally intended to apply to multi-component chalcogenide glasses .

I-2-3 : Davis – Mott Model (14) :

This model proposed that the mobility edges for electrons and holes lie at E_c and E_v , Fig (1-5) . A stronger distinction is made between localized states which originate from lack of long – range order and other which are due to defects in the structure . The first kind of localized states extend only to E_A and E_B in the mobility gap , the defect states form longer tails but of insufficient density to pin the Fermi-level . Moreover , the others propose a band of compensated level near the gap center in order to pin the Fermi-level and the account for the behaviour of the a.c conductivity . The center band may be split into two bands .

1-2-4 : Marshell – Owen Model (15) :

In this model, shown in Fig.(1-6) , the position of the fermi-level is determined by bands of donors and acceptors in the upper and lower halves of the mobility gap respectively . The concentration of donors and acceptors adjust themselves by self compensation to be nearly equal , so Fermi-level remains near the gap center . At low temperature it moves to one of the impurity bands because self compensation is not likely to be complete .

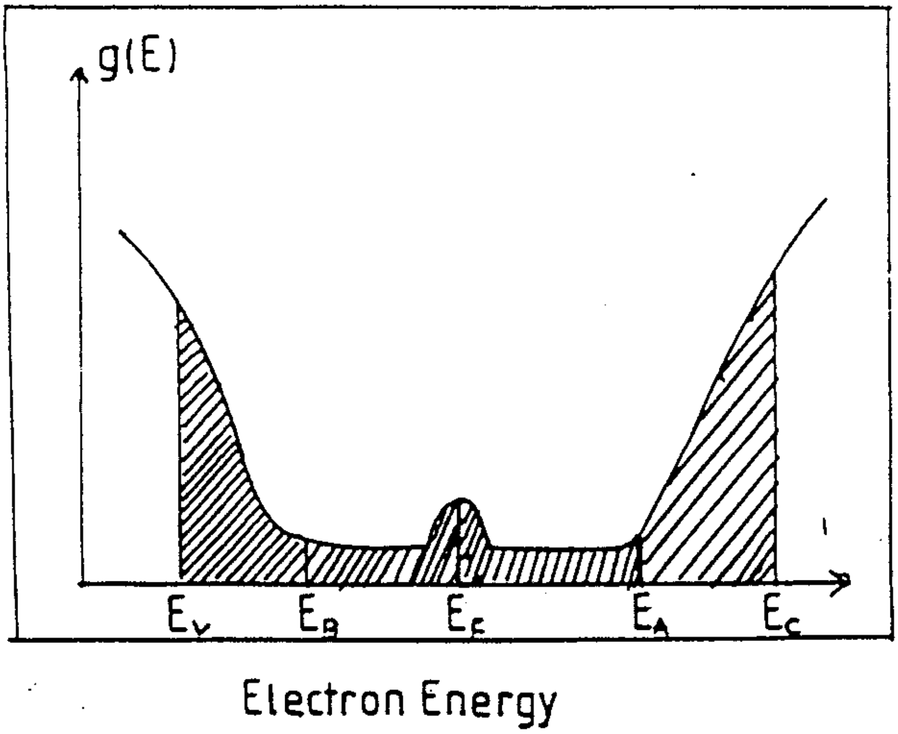

Fig. (I-5) : **Davis-Mott band model.**

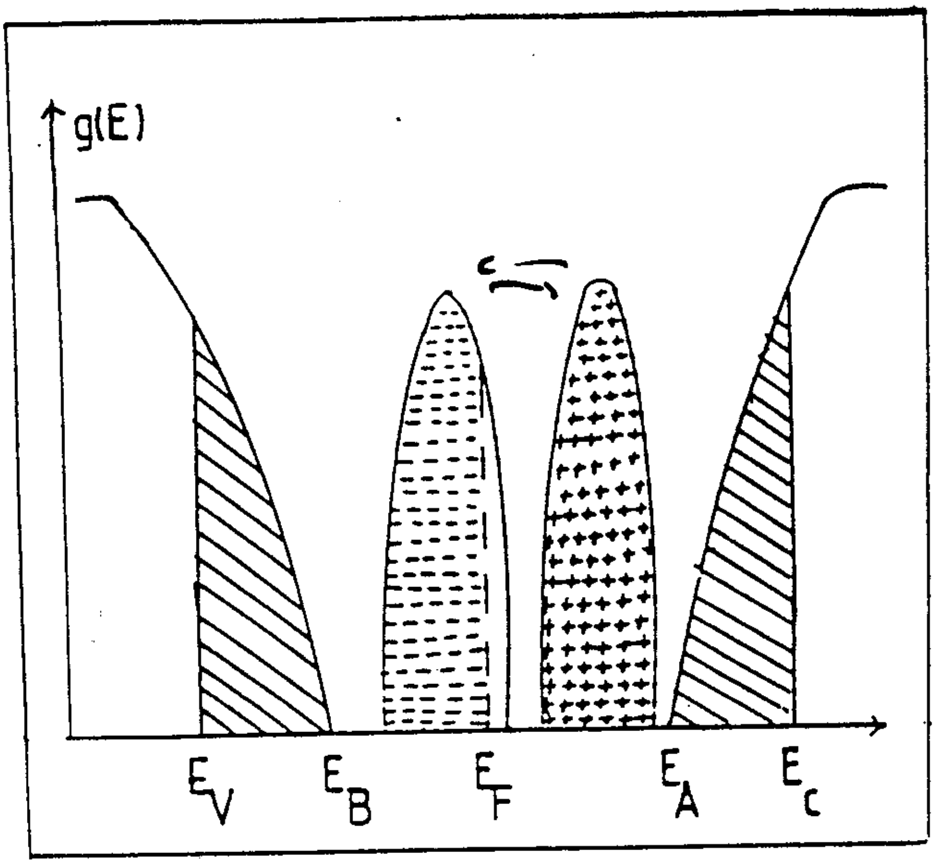

Fig. (I-6) : **Marshall-Owen band model.**

I-2-5 : Small Polaron Model :

The small polaron model was proposed by Emin(16) . According to this model , the charge carries enter the self – trapped (small polaron) state via polarization of the atomic lattice .

The field effect screening is accomplished by redistribution of small polarons within the space charge layer .

The small density of polarons can be calculated , its thermal activation energy being the separation in energy of the polaron band from the Fermi – level .

The difference between its energy and conductivity activation energy is equal to the hopping energy for polaron movement . The temperature dependence of the field effect is therefore capable of testing the small polaron model in the range where the field effect screening is controlled by polarons .

I-2-6 : Sharp Band Edge Model :

This model is useful for describing oxide glasses and semi-insulating materials (17) , Fig. (1-7) shows that the molecular solids and tight binding , semi-insulating materials with large band gaps have electronic structures which are relatively insensitive to disorder. In these materials tail states are negligible and a band model not significantly different from that of crystals with sharp band edges is appropriate . Since the molecular units are well defined entities one expects that the energies of localized defect states fall into rather narrow energy ranges deep in the gap . Because the energy to create a defect state is of the order of the band gap . Their number will be

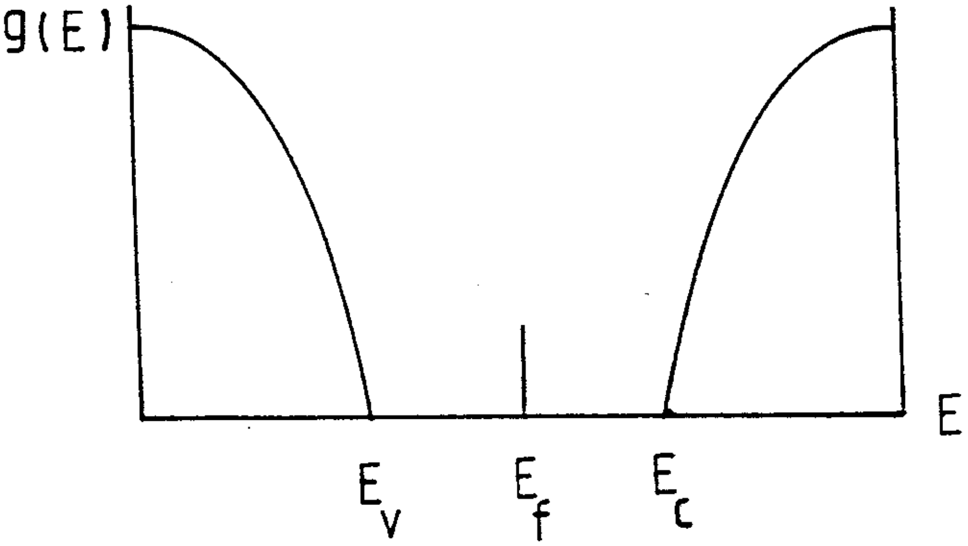

Fig. (I-7) Sharp band edge model.

small and self compensation as well as association of donor and acceptor type defects are energetically favored .

I-3 :D.C Electrical Conductivity Of Amorphous Semiconductors :

On the basis of principles suggested by Mott and Davis(18) , a fairly narrow band of localized states (< 0.1 eV) is assumed to exist near the center of the gap , of sufficiently high density to effectively pin the Fermi energy over a wide temperature range . Thus conduction is extrinsic rather than intrinsic . The origin of the states is speculative , but they could concreivably arise from some specific defect characteristic of the material .

With the above model(14) , there can be three processes leading to conduction in amorphous semiconductors . Their contribution to the total conductivity will change markedly in different temperature ranges :

a) conduction due to carriers excited beyond the mobility shoulders into extended states. If the main current is carried by holes they expect,

$$\sigma = \sigma_o \exp . [- (E_F - E_v) / k_B T] \qquad (1\text{-}1)$$

where k_B is Botzmann's constant and The pre-exponential factor σ_o is expected to given by :

$$\sigma_o = eN (E_v) k_B T \mu_o \qquad (1\text{-}2)$$

Since σ_o is not expected to be temperature dependent, the mobility in extended states μ_o is proportional to $1/T$.

A plot of $\ln\sigma$ against $1/T$ yield a straight line if ($E_F - E_v$) is a linear function of T over the temperature range measured . If

$$E_F - E_v = E(0) - \gamma T$$

where γ the temperature coefficient of $(E_F - E_v)$, then the slope of such a plot will be $E(0) / k_B$, and the intercept on the σ axis will be:

$$\sigma_o \exp(\gamma / k_B)$$

b) conduction due to carriers excited into the localized states at the band edges i.e at E_A or E_B. Again if the main current is carried by holes, and conduction is by hopping, then

$$\sigma = \sigma_1 \exp.[-(E_F - E_B + \Delta w_1) / k_B T] \qquad (1\text{-}3)$$

where Δw_1 is the activation energy for hopping and E_B is the energy at the band edge. An estimate of σ_1 is not easy, but is expected to be a factor of $10^2 - 10^4$ less than σ_o, due to partly to an effective density of states lower by a factor $(E_B - E_v)/ k_B T$, but mainly to a lower mobility μ_1. Only if μ_1 does not fall off too rapidly between E_v and E_B will the current be carried at E_B and a straight line be obtained on a plot of $\ln\sigma$ against $1/T$.

c) conduction due to carriers hopping (tunneling) between localized states near the Fermi energy. This is the process analogous to impurity conduction in heavily doped semi-conductors, then:

$$\sigma = \sigma_2 \exp(-\Delta w_2 / k_B T) \qquad (1\text{-}4)$$

where Δw_2 is the hopping energy of the order of half the width of the defect. Since the density of states near E_F is probably smaller than near E_A or E_B. They emphasize here that a straight line in a plot of $\ln\sigma$ against $1/T$ expected only if hopping is between nearest neighbours. As the temperature is lowered, it may become favourable for the carriers to tunnel to more distant sites, Δw_2 will fall, and ultimately the conductivity is expected to behave like :

$$\ln\sigma = A - B\,T^{-1/4} \qquad (1\text{-}5)$$

The total conductivity for all processes is obtained as an integral over all available energy states . Thus for states above E_F , assuming Boltzmann statistics .

$$\sigma = e\int N(E)\,\mu(E)\,F(E)\,dE \qquad (1\text{-}6)$$

where F(E) is the Boltzman distribution function, Fig.(1-8) shows schematically the variation of N(E) , μ(E) and F(E) , with E is the energies above E_F , and the manner in which σ(E) may vary with temperature . This is also shown on a plot of $\ln\sigma$ against 1/T in Fig.(1-8) . If the density of defect states is high , then process (b) will not dominate in any temperature range and a direct transition from (a) to (c) will result .

1-4 : Ionic Conduction(9) :

Ionic conductivity involves the long range migration of ionic charge carriers . The charge carriers through the glass under the driving force at an applied electric field will be the most mobile ions in the glass and therefore for silicate glasses , are usually +1 valence cations moving in an immobile SiO_2 based matrix . The electric force in the cation serves to perturb its random thermal motion by increasing the probability of a transition in the direction of the applied field . This behaviour can be described by considering the two schematic potential energy wells shown in Fig.(1-9) . The

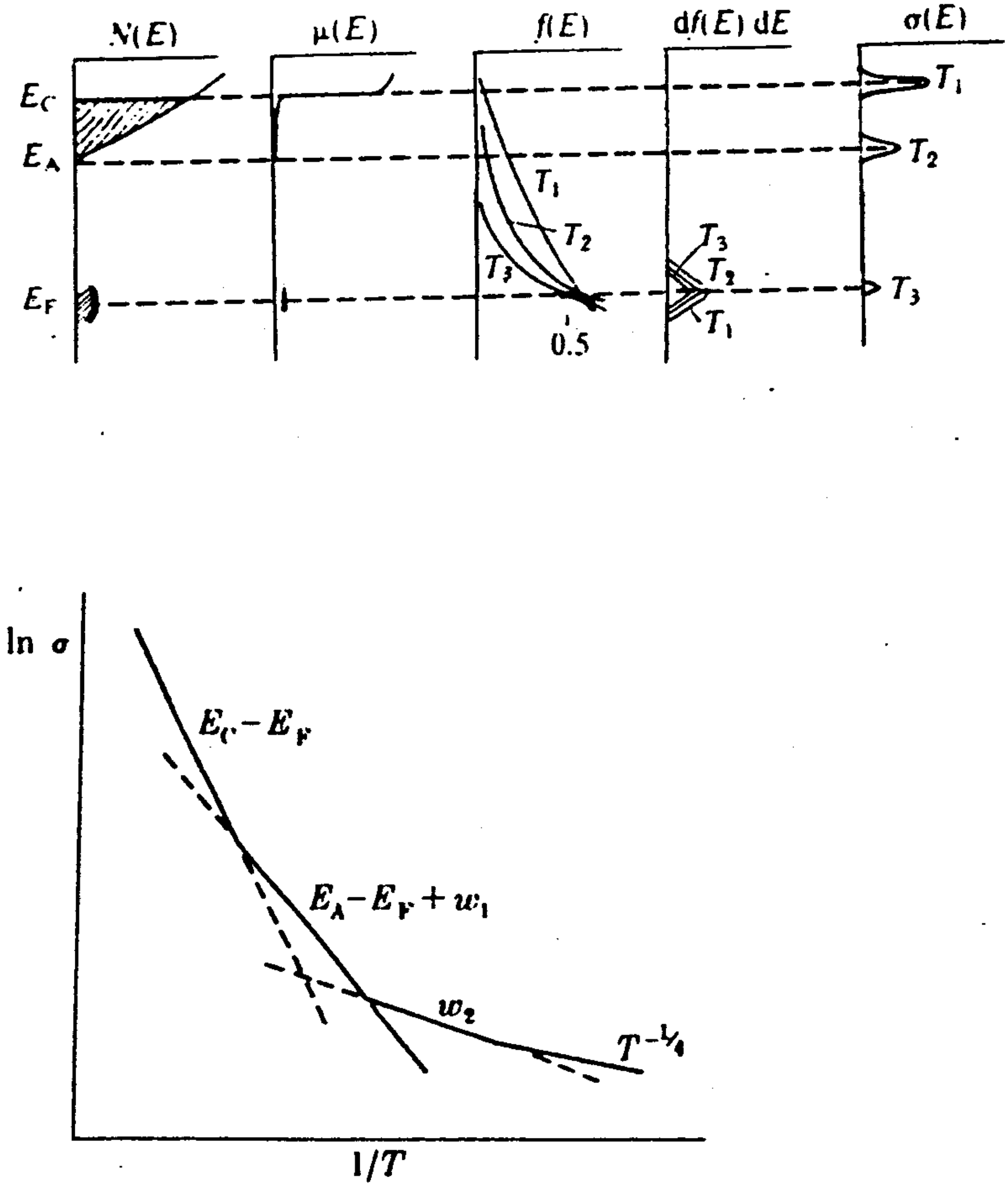

Fig. (I-8) The activation energies associated with various processes potential barrier w represents the maximum barrier in the path of least resistance in the glass .

Consider that the ions move in one dimension parallel to the x axis jumping over the potential barrier w . The probability that an ion will move to either the right or the left is :

$$P = \alpha\,(k_BT / h)\,\exp(-w / k_BT) \qquad (1\text{-}7)$$

where α is an accommodation coefficient related to the irreversibility of the jump ; k_BT/h is the vibrational frequency of the ion in the well, k_B is Botzmann's constant , and T is the absolute temperature . When a field E is applied , the ion coordinations are slightly distorted within the glass structure and the potential barrier to the ion motion is slightly shifted as shown in Fig.(1-9) . The field will lower the potential barrier on the side in the direction of the field and raise it on the other side by an equivalent amount . If the distance between the two wells is (b) the potential on the right side will now be smaller by an amount , $\frac{1}{2}\,zEb = \frac{1}{2}\,F\text{`}b$ , F` is the force on the ion and z is the valence of the ion .

Therefore , the probability of motion to the right is :

$$P^+ = \tfrac{1}{2}\,\alpha\,(k_BT / h)\,\exp[-[w - \tfrac{1}{2}F\text{`}b] / k_BT] (1\text{-}8)$$

or $$P^+ = \tfrac{1}{2}\,P\,\exp[+F\text{`}b / 2k_BT]$$

The probability of motion to the left is thus :

$$P^- = \tfrac{1}{2}\,\alpha\,(k_BT / h)\,\exp[-[w - \tfrac{1}{2}Fb] / k_BT] \qquad (1\text{-}9)$$

Or $$P^- = \tfrac{1}{2}\,P\,\exp[-F\text{`}b / 2k_BT] \qquad (1\text{-}10)$$

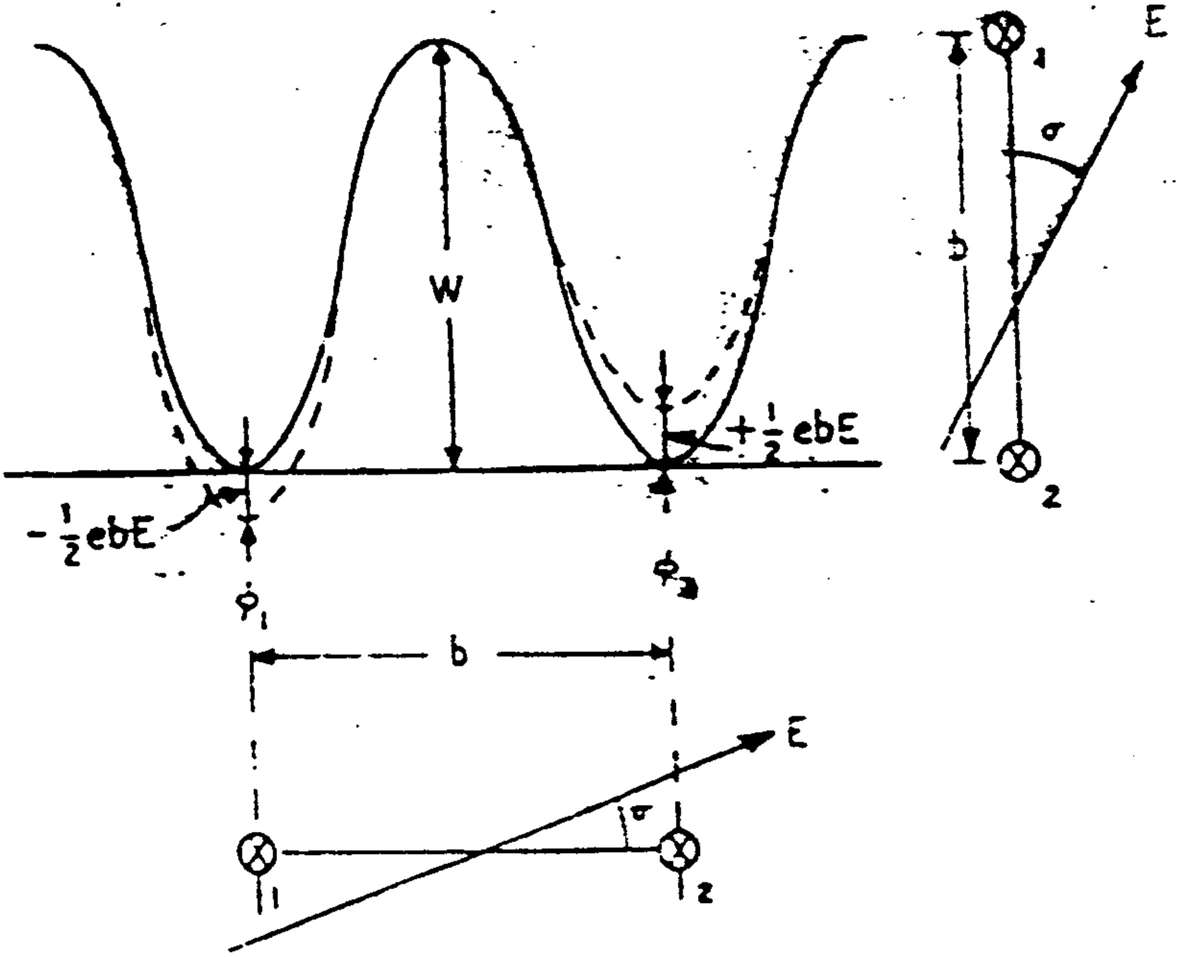

Fig.(I–9): The schematic potential energy wells.

Consequently the positive transitions will be more frequent than the negative and therefore will be an average drift velocity to the right in the direction of the field .

The mean velocity of the drift motion is :

$\bar{V} = b (P^+ - P^-) = ½ Pb [\exp (+ F`b/2k_BT) - \exp (- F`b/2k_BT)]$

$\bar{V} = b P \sinh (F`b/2k_BT)$ (1-11)

The electric field merely directing the random diffusion of ions that occut spontaneously at any temperature , T . The field does not pull the ions of the wells , as long as the field strength is much smaller than k_BT , i.e. , $½ F`b << k_BT$, then sinh can replaced by the argument and the drift velocity can be expressed as ,

$\bar{V} = b^2 pF`/2k_BT$ (1-12)

In the case of very large field strengths exist , the first term in sinh will dominate and :

$\bar{V} = \text{const. } \exp (bF` /2k_BT)$ (1-13)

At room temperature bF` is small compared with k_BT up to field strength 10 V/cm . Therefore , the current will be proportional to the field strength in agreement with Ohm's law :

$J = nze\bar{v}$ $n = 0$ of ions / cm^3 , $q = ze$ (1-14)

So , $J = nze b^2 pF`/ 2k_BT = nz^2 e^2 b^2 pE /2k_BT$ (1-15)

and substituting ,

$P = (\alpha k_BT /h) \exp[-w/k_BT]$ and $W = \Delta F_{DC} / N$ (1-16) where ΔF_{DC} is the change in free energy for dc conduction and N is Avagadro's number.

yields $J = (n \alpha z^2 e^2 b^2 E / 2h) \exp - (\Delta F_{DC}/RT)$ (1-17)

Therefore, the electrical resistance of glass :

where R is gas constant

$$R = E/J = (2h/n \alpha z^2 e^2 b^2) \exp (\Delta F_{DC}/RT) \quad (1\text{-}18)$$

or $$G = 1/R = (n \alpha z^2 e^2 b^2)/2h \exp (-\Delta F_{DC}/RT) \quad (1\text{-}19)$$

which is similar to the Rasch-Htinrichsen law of electrical resistiveity of glass discovered empirically(20) :

$$\text{Log}\, \rho = A + B / T$$

The final expression for the conductance :

$$\text{Log}\, G = \log [(n \alpha z^2 e^2 b^2/2h) + (\Delta S/R)] - \Delta H_{DC}/RT) \quad (1\text{-}20)$$

where ΔH_{DC} is the enthalpy and ΔS is the entropy.

I-5 : High Field Conduction (21) :

Consider first a solid containing only donor-like of an activation energy ϕ, for emission of carriers into the conduction band. The positively charged nucleus of the donor center appears as a coulombic potential well of energy :

$$\phi (r) = - e^2 / 4 \pi \varepsilon r \quad (1\text{-}21)$$

As shown in Fig. (I-10), this energy is " seem " by the electron nearest to the donor center, weather this electron is actually on the center or at some distance from it. When once accuptid by an electron, however, the center appears neutral to any other electrons. Similarly, an ionized center would be screened effectively from any electrons more distance than the nearest one.

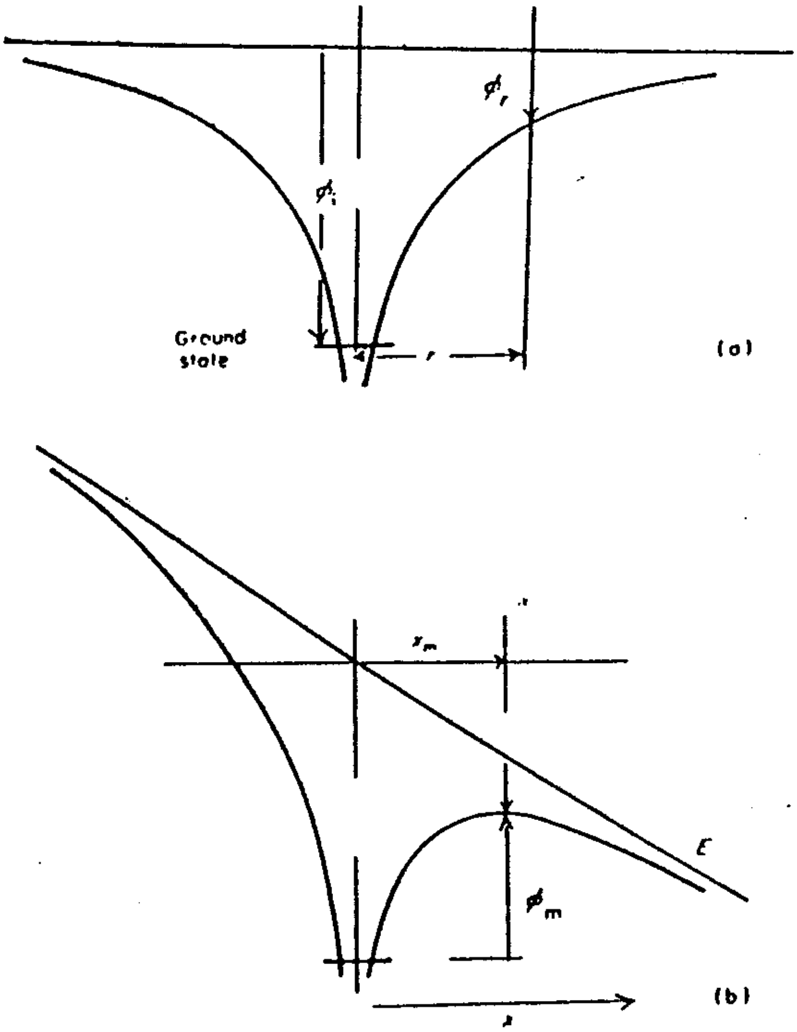

Fig.(I–10): The coulombic pontential of a donor center :
(a) in absence of external field (b) with an external field producing a lowering of the carrier for escape of the electron.

In the presence of an external field E , the potential energy becomes :

$$\phi(r) = -e^2/4\pi\varepsilon r - eEr\cos\theta \qquad \text{(I-22)}$$

where θ is the angle between the radius vector r and the electric field . Confining them attention at present to the field direction, x , the maximum of potential is found to be :

$$\phi_m = \phi_i - e\beta E^{1/2} \qquad \text{(I-23)}$$

where the Poole – Frenkel constant : $\beta = (e/\pi\varepsilon)^{1/2}$

and the maximum occurs at a distance : $X_m = \beta/2E^{1/2}$

The maximum potential in any other direction θ is :

$$\eta_m(\theta) = \phi_i - e\beta(E\cos\theta)^{1/2} \qquad \text{(I-24)}$$

The probability that an electron confined to a coulomb well immersed in a lattice of temperature T will receive an amount of energy η in excess of its ground state may be expressed in the form :

$$P(\eta) = BT^b \exp(-\eta/k_BT) \qquad \text{(I-25)}$$

where B is constant independent of temperature and T^b indicates a possible temperature dependence which is not expected to be strong .

Allowing for the usual density of states in the conduction band and assuming that the electron will have a constant probability of transition into any conduction band states at its own energy , they obtain the probability of emission into the solid angle dΩ .

$$ds = 2\pi(2m^*/h^2)^{3/2}\exp(-\eta_m/k_BT)\,BT^b(k_BT)^{3/2}\,d\Omega \qquad \text{(I-26)}$$

They note that $d\Omega = 2\pi \sin\theta \, d\theta$ and finally obtain the total probability of emission into the hemisphere in the direction of the field .

$$S = c\, T^{b+3/2} \exp(-\phi_i / k_B T)\, [\, e^{\gamma} (\gamma - 1) + 1) / \gamma^2] \qquad \text{(I-27)}$$

where $\gamma = e\, \beta\, E^{1/2} / k_B T$

The probability of emission becomes approximately

$$S = (k_B/e) c T^{b+3/2} \exp(-\phi_i/k_B T)(\beta E^{1/2})^{-1} \exp(e\beta E^{1/2}/k_B T) \quad \text{(I-28)}$$

The current flowing in the material will depend on the number of available centers N , and on the distance traveled by each carrier after emission . Here they have to consider three possibilities :

i) The carrier is not recaptured in the material but travels to the anode and is lost .

ii) The carrier travels a distance L which is proportional to the electric field before being recaptured in an empty donor .

iii) The carrier travels a fixed distance L independent of the electric field , for example , to the nearest empty donor downstream .

For the model discussed here in which the probability of emission in any given direction depend only on the height of the barrier in that direction .

I-6 : Switching and Memory Characteristics :

Switching properties , first reported by Ovshinsky(22) in chalcogenide glasses . This switching phenomenon is expressed by a particular electrical behaviour of the material when it is subjected to a strong electric field .

The current – voltage characteristics of amorphous semiconductor Fig.(I-11) could be divided into three stages$^{(23)}$:

1: *The Off - State* :

In this state , the current voltage relation show firstly at low voltage (ohmic region) and after that the current increases exponential with the increase of the voltage . This behaviour is limited at a certain point called the turn – over point (T.O.P) , at which the values of voltage , current and resistance are called threshold (V_{th} , I_{th} and R_{th} respectively).

2 : *Negative Resistance State* :

During this region the current increases rapidly as the voltage decreases accompanied by a nucleation process negative resistance state , and it ends at the beginning of the third state . A complete crystallization process occurs in the filament and , its resistance becomes very low .

3 : *On - State* :

This state occurs at (I_c , V_c) , where I_c is the crystallization current and V_c is the crystallization voltage . The material in this state is in the crystalline form , Characterized by a low resistance . So it is called " ON – State " .

Fritzsche$^{(24)}$ has been classified the switching and memory phenomena into the following five types , Fig.(1-12) .

a) The negative resistance device :

This device has an I-V Characteristic which is retraceable except for some hysteresis which are observed when the current is

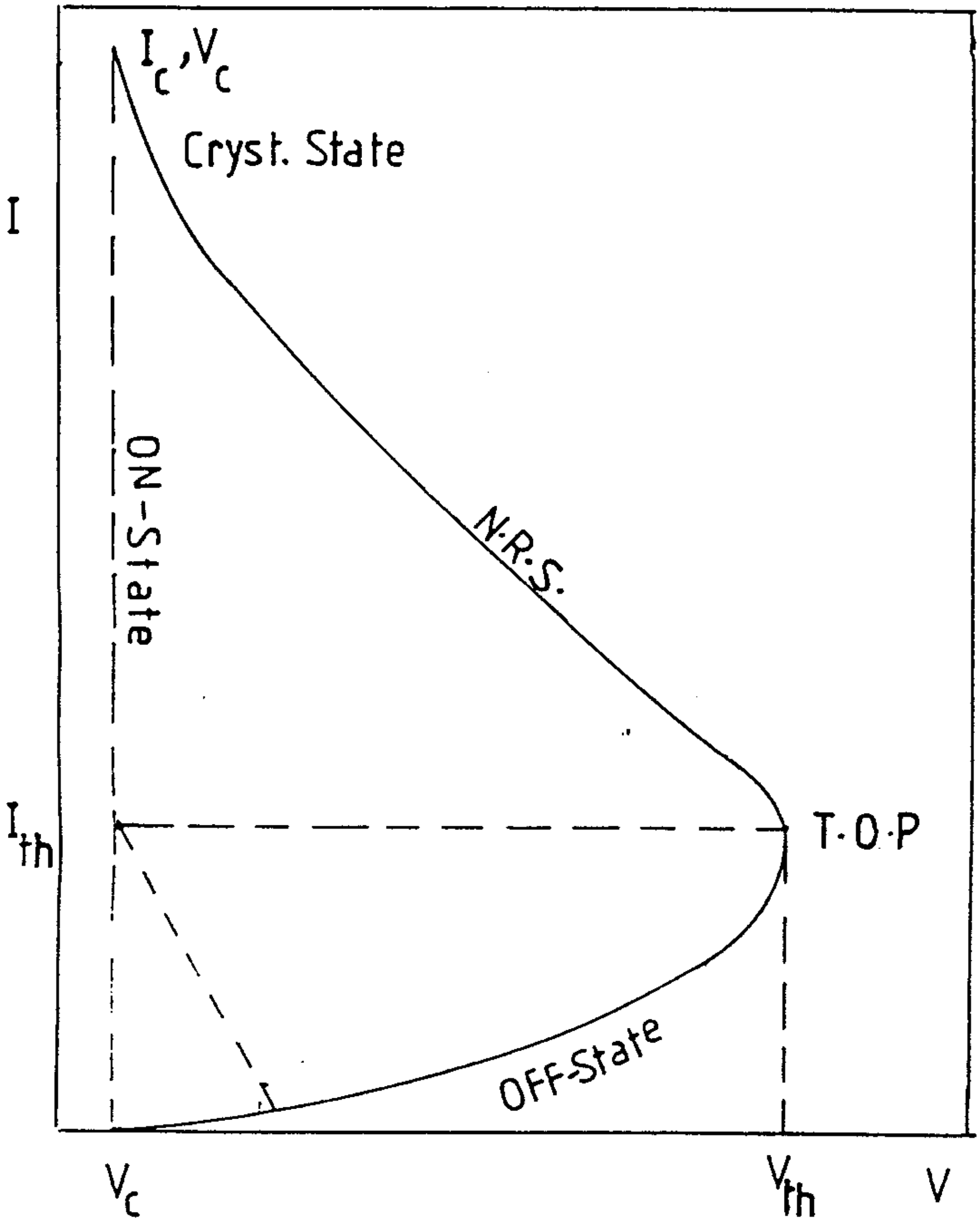

Fig. (I-11): Typical (I-V) curve.

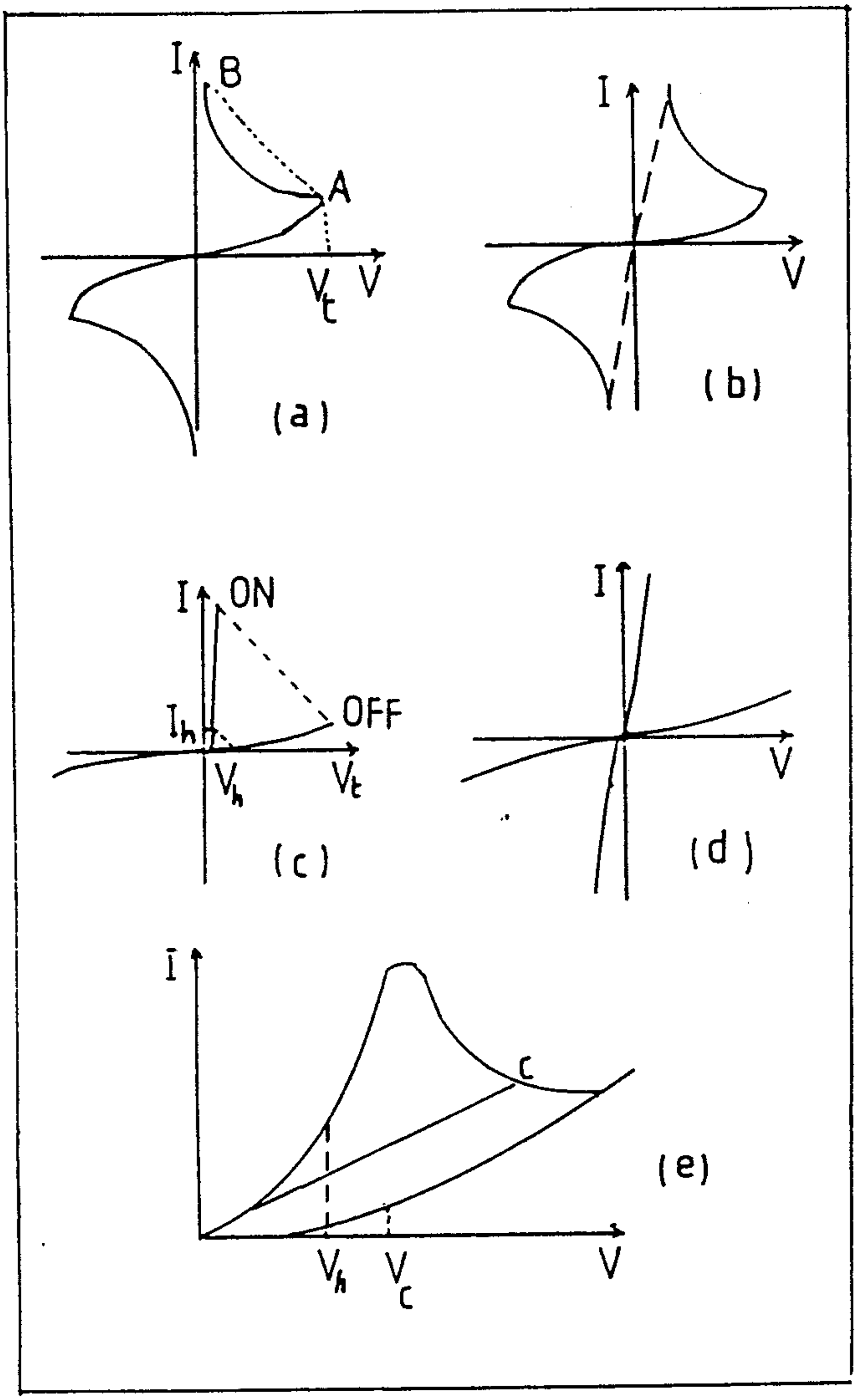

Fig. (1-12)
Classification of switching and memory characteristics;
(a) N.R.D. (b) N.R.D. with memory. (c) switching device
(d) switching device with memory(e) V.C.N.D. with memory.

changed too rapidly for maintaining thermal equilibrium . By using a small resistance RL this negative resistance device can be made to switch from point A where the load line is tangential to the I-V curve to the point of intersection (B) of the load line and the Characteristic .

b) The negative resistance device with memory :

It has two stable states . The first state resembles that of case (a). The second is conductive . It is established at higher currents and remains without decay . The first state can be reset by increasing the current above a certain value and switching it off rapidly .

c) Switching device :

This device has no stable operating point between the high resistance off state and the conductive ON state of which the device switches when the voltage exceeds the threshold voltage , Vth . The device switches to its original Off state when the current is decreased below holding current (I_{th}).

d) The switching device with memory :

It has two stable states . The high resistance state and the mode of switching resemble device (c) . The conducting ON state , which is established after switching by means of setting current , remains even if the voltage is removed entirely .

e) The voltage controlled negative resistance with memory :

As shown in (C) . The devices pass through a negative resistance region above a voltage v_c to a state of high resistance . The I-V Characteristic is retraced when the voltage is changed slowly . However , the high resistance state is retained at low voltages when the voltages is reduced rapidly .

1-6-1 : Heterogeneous Models :

Heterogeneous models(17) suggest that the forming process creates in the filament region a new material whose properties have little relation to those of the original material . The new material usually does not behave like an homogeneous amorphous semiconductor . After such a forming process the device usually exhibits a lower threshold voltage and a lower off resistance than the virginal device(25-27) .

Bosnell and Thomas (28) were able to isolate the filament region of formed device which were made of Te rich chalcogenide alloy glasses . They explain switching and ON – State of the threshold and memory devices in the following manner . During the first switching operations , oriented crystals of Te phase separate from a glassy matrix as a result of the relatively high temperature and electric field in the region of the current filament . These crystals remain isolated in the formed Off – State .

The ON – State is stabilized by the formation of a connected crystalline matrix of high conductivity . In memory switches this connected crystalline matrix remains even when the current is removed after a lock-on period .

It can be reset into the formed state by a current pulse which revivifies a sufficient amount of material to render the remaining crystals isolated . In threshold devices the connected crystalline ON-State is less stable and returns to the formed Off-State when the current falls belwo the minimum holding current .

1-6-2 : Thermal and Electrothermal Theories :

The physical process is essentially the following : Joule heating raises the temperature inside the semiconducting material . The resulting increase in conductivity allows more current to flow through the heated regions with the consequence of enhanced Joule heating and an increased concentration of the current flow in the heated region . A new stationary state is established when the heat conducted away from the current filament equals the Joule heat generated in that region .

The establishment of a stationary state depends on the external limiting of the current and the heat flow to the environment . Then the time dependent I-V characteristic is obtained as a solution , with the appropriate boundary conditions of the heat transport equation :

$$\nabla . (k \nabla T) + j^2 / \sigma = C_v \, dT / dt \qquad \text{(I-29)}$$

the charge conservation equation $\nabla . j = -d\rho / dt$,

where k (T) is the thermal conductivity , σ (T) is the electrical conductivity , ρ is the charge density and C_v the heat capacity .

The work of Kroll(29) presents the most through theoretical analysis of the thermal breakdown process . The principle results of this study are no negative resistance region and hence no switching occurs when the electrodes are perfect heat sinks and the reason for this is simply that the semiconducting material adjacent to the electrodes remains cold and its high resistance prevents the appearance of a negative resistance region .

In a number of studies (30,31) the heat was assumed to flow perpendicular to the current instead between the electrodes . A negative resistance region is then obtained because the entire current path between the electrodes heats up in this case . This heat flow geometry however appears unrealistic for a thin film device because the thermal conductivity of a metal .

According to Owen(32) the device current I is a function of temperature and volt .

$$I = v \, . \, \sigma = f(v, T) \qquad \text{(I-30)}$$

And the turn – over occurs when :

$$(\delta E / \delta T)(\delta \sigma / \delta v) = 1 \qquad \text{(I-31)}$$

The turn – over temperature T\` is :

$$T` = T_a + k_B T_a^2 / \Delta E \qquad \text{(I-32)}$$

where T_a is the ambient temperature .

The turn – over voltage is :

$$V = 0.6 T_a (k_B D / \Delta E \, \pi \, a^2 \sigma_o)^{1/2} \exp(\Delta E / 2 \, k_B T_a) \qquad \text{(I-33)}$$

Many authors (33-36) considered an electronic correction terms to the Electrothermal theories . Based on the assumption that the breakdown voltage and the ON – impedance are greatly reduced when the conductivity of the semiconductor is assumed to raise with increasing field strength or , when space charge injection or tunneling process are introduced to reduce the impedance of the cold layers near the electrode because of the field enhanced conductivity , the cold layer effect is diminished in Electrothermal theories and a negative resistance region can be obtained even with perfectly heat sinking electrodes and at lower voltages .

1-6-3 : Electronic Theories :

Because of the large field enhancement of the conductivity before breakdown one suspects the electric processes such as carrier avalanche , double injection , or high field tunneling , can initiate breakdown process before the thermal or Electrothermal breakdown proceeds . When switching is initiated by an electronic process , a current channel will form upon switching and considerable temperature rise will occur in this channel because the Joule heat is dissipated in rather small volume .

In the ON – State of the threshold switch most of the voltage drop occurs at one or both electrodes , the rest of the semiconductor is well conducting and almost field free . This field distortion indicates the presence of space charges adjacent to the electrodes and a region free of space charge in the center .

The electronic switching model assume the following points :

i- An excess electron and hole concentration is established by field dependent processes in the bulk or by injection from the electrodes .

ii- These excess concentrations in the bulk can be sustained after switching by high field regions near the contacts . These excess concentration , which cause the bulk to be highly conducting (but neutral) , can be described by quasi-fermi levels for electrons and holes which split a part from the equilibrium fermi-level . The equilibrium time τ_o for two quasi – fermi levels to return to the equilibrium level after removal of the voltage is assumed to be long .

1-7 : The A.C Conductivity in Amorphous Semiconductors :

In many amorphous semiconductors and insulators a.c conductivity invariably has the form :

$$\sigma(\omega) = A\,\omega^{s} \qquad \text{(I-34)}$$

where A is a constant depends on temperature and s is the temperature dependent parameter, is generally less than or equal to unity . There are three mechanisms of charge transport that can contribute to a direct current in amorphous semiconductors . They can all contribute to the a.c conductivity as follows :

1-7-1: Transport by carriers excited to the extended states near E_c or E_v.

For these They(37,38) might expect that $\sigma(\omega)$ would be given a formula of the Drude type ,

$$\sigma(\omega) = \sigma(0) / (1+\omega^2\tau^2) \qquad (I\text{-}35)$$

The time of relaxation τ will be very short ($\simeq 10^{-15}$ Sec.) and a decrease in $\sigma(\omega)$ as ω^{-2} is not expected until a frequency = 10^{15} Hz is reached . It is sufficient to state here that in the electrical range of frequencies (up to , 10^7 Hz) no frequency dependence of the conductivity associated with carriers in extended states is expected .

1-7-2 : Transport by carriers excited into the localized state at the edges of the valence or conduction band :

A similar dependence on frequency to that derived under degenerate condition 1-7-3 and thus as ω^s where $s < 1$ when $\omega < \nu_{ph}$. The temperature dependence of the a.c conductivity should be the same as that of the carrier concentration at the band edge , so that for the conduction band is should increase as : $\exp[-(E_A - E_F)/k_BT]$

1-7-3 : Hopping transport by electrons with energies near the Fermi level , $N(E_F)$ is finite :

There have been several theoretical treatments of $\sigma(\omega)$ for this mode of conduction . $\sigma(\omega)$ should increase with frequency in a manner similar to that for process 1-7-2 . However , the exponential dependence on the temperature will be absent , and $\sigma(\omega)$ should be proportional to T. if (k_BT) is small compared with the energy range over which $N(E_F)$ may be taken as constant , and independent of T if

(k_BT) is larger than the width of some well-defined defect band in which E_F lies in the range of k_BT .

The analysis of observed results has been given by Mott and Davis (18) using the formula given by Austin and Mott (36) namely :

$$\sigma(\omega) = (\pi/3)\, e^2\, k_BT\, [\, N(E_F)]^2\, \alpha^{-5}\, \omega\, [\ln(\, \nu_{ph}/\omega)]^4 \qquad \text{(I-36)}$$

This analysis also have been discussed by Pollak(37) and by Butcher(38) and they obtained a similar formula with a slightly different numerical factor , replacing ($\pi/3$) in eq. (I-36) by ($\pi^3/96$) or ($3.66\, \pi^2/6$) .

The frequency dependence can be written as :

$\sigma(\omega)\ \alpha\ \omega^s$, where s is a weak function of $\omega \ll \nu_{ph}$ and considering that :

$$s = d\, [\, \ln (\omega \ln^4 (\nu_{ph}/\omega))\,] / d\, (\, \ln \omega\,) \qquad \text{(I-37)}$$

$$= 1 - 4 / (\, \ln (\nu_{ph}/\omega)$$

A schematically illustration of the frequency dependence of the conductivity expected for the three conduction mechanisms is shown in Fig.(1-13) for the two hopping process (1-7-2 and 1-7-3) , $\sigma(\omega)$ increases as ω^s .

I-8 : Dielectric Properties :

Dielectric properties comprise the non-long range conducting electrical characteristics of glass . Dielectric responses result from the short range motion of charge carriers under the influence of applied field . The motion of the charge leads to the storage of electrical energy and the capacitance of the dielectric .

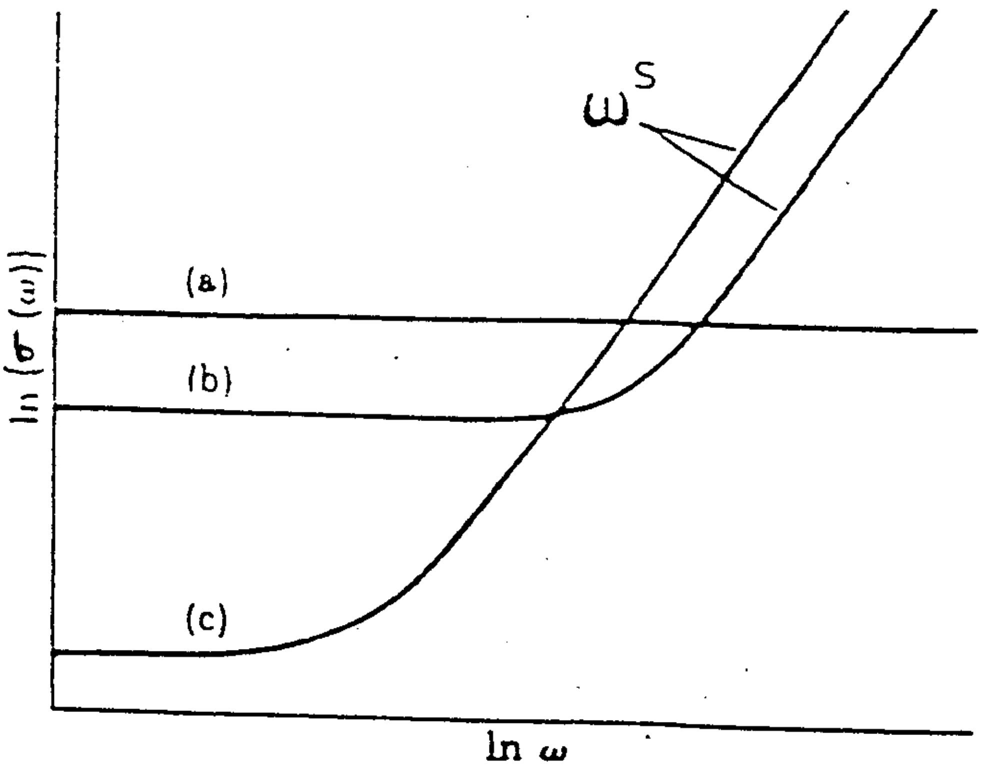

Fig. (I-13) Schematic illustration of the frequency dependence of conductivity for the three modes of conduction

I-8-1 : Polarization in Glass :

There are four primary mechanisms of Polarization in glass . Each mechanism involves a short range motion of charge and contribute to the total Polarization of material . The Polarization mechanisms include(39) :

1- Electronic Polarization (P_e) :

2- Ionic Polarization (P_i) :

3- Oriantational Polarization (P_o) :

4- Interfacial Polarization (P_s) :

- Electronic Polarization is due to the shift of the valence electron could of the ions within the material with respect to the positive nuclei . This mechanism of Polarization occurs at a very high frequency (10^5 Hz) , At frequencies in the range (10^{12}-10^{13} Hz), atomic or ionic Polarization occurs . Atomic Polarization is the displacement of positive and negative ions in a material with respect to each other .

In the sub-infrared range of frequency , orientation Polarization contributes to the dielectric properties of glass . Orientational Polarization also referred to in some texts as dipolar Polarization , involves the perturbation of the thermal motion of ionic of molecular dipoles , producing a net dipolar orientation in the direction of the applied field , the last polarization mechanism , interfacid or space charge polarization occurs when mobil charge carriers are impeded by a physical barrier that inhibits charge migration .

I-8-2 : Dielectric Constant of Glasses :

The dielectric constant of glasses , as expected decreases with increasing frequency . However , the variation over wide ranges of frequency is quite small . The dielectric constant increases slightly with increasing density of glasses . This is attributed to the fact that dielectric constant is direct measure of Polarization per unit volume and that for a denser glass there are more electrons and ions to Polarize . This is obviously an oversimplified assumption , since the rigidity of the overall glass must also be considered . At elevated temperature the glassy network relaxes and ionic motion becomes easter . Thus dielectric constant should increase with increasing temperature . This increase is also expected to be more pronounced at low frequencies , since the ions have more time to participate in the motion . These expectations have been repeatedly confirmed for a variety of glasses (40) .

I-8-3 : Dielectric Losses in Glass :

Stevels (41) has proposed a spectrum of losses to describe the behaviour of glasses in a periodic field over the range 1 to 10^{14} Hz as shown in Fig.(1-14) .

The four losses represented by the dashed lines in Fig.(1-14) are conduction losses , Dipoler relaxation losses , deformation losses and vibration losses .

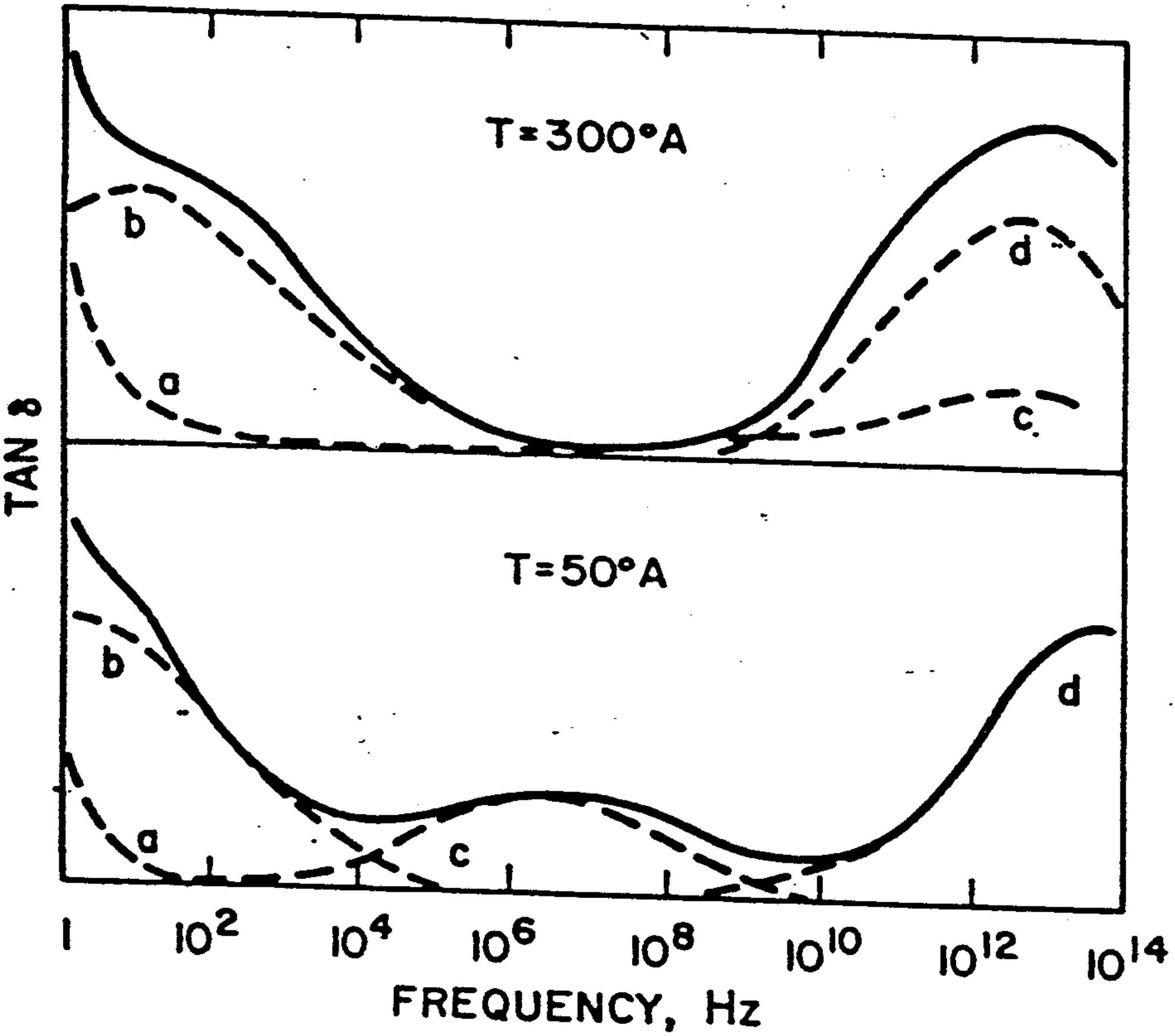

Fig.(I–14): Spectrum of dielectric losses according to Stevels.

a: Conduction losses :

Conduction losses occur at low frequencies and are attributed to the migration of ions over large distances . They are obviously related to d.c conductivity. If a condenser containing a glass dielectric is represented by a simple circuit of a resistance R in parallel with a capacity c . Then in an a.c field of angular frequency ω :

$$\tan \delta = 1 / \omega R c \qquad \text{(I-38)}$$

tan δ is the inversely proportional to the frequency . Except at very low frequencies or at high temperatures , conduction losses are small. At frequencies in excess of 10^2 Hz this type of losses is generally negligible .

b: Dipole relaxation losses :

These losses are attributed to motion of ions over short distances . If a spectrum of energy barriers exists in the random glassy network , then an ion might be able to move over relatively short distances and be stopped at a high-energy barrier .

In the a.c field such ions will only be able to oscillate between two high-energy barrier separated by a short distance . It is , of course, assumed that lower barriers exist between the tow limiting ones . Thus an additional loss is operative at low frequencies .

The time required for such ions to oscillate is of the order of 1 sec. at room temperature , and this is termed the relaxation time τ for that process . Thus at frequencies of about 1 Hz the loss factor is maximum . At much lower frequencies $\omega << 1/T$, the loss have adequate time to move and do so at low fields and hence losses are low . At ω >> 1/T , the field is too rapid for the ions to follow , and hence losses are again low .

c: Deformation losses :

Deformation losses are associated with even more limited ionic motions . For example in fused silicate , for instance , this type of loss can be attributed to the lateral oscillation of an oxygen ion between two silicones . At low temperatures , maximum loss would occur at about 10^6 Hz , and at room temperatures at about 10^{13} Hz .

d: Vibration losses :

All the ions in a glass can vibrate about their equilibrium position at some frequency dependent on their mass and the potential wells they are in . Whenever the applied electric field alternates at a frequency similar to that of one of vibrating ions , the ions are excited to high resonant amplitudes, thus leading to vibration losses . The maximum of such losses is expected therefor to occur at about 10^{13}Hz . Measurements of vibration losses are scarce .

I-8-4: The Effect of Frequency And Temperature On the Dielectric Loss :

Dielectric relaxation studies are important to understand the nature and the origin of dielectric losses which , in turn , may be useful in the determination of structure and defects in solids .

Also , the study of frequency dependent electrical conductivity of amorphous compounds are important to elucidate the mechanisms of conduction in these substances (37) . This led to adapt and to elaborate models allowing the electronic properties of several substances to be described [(42)] Generally , such solids are correctly represented by localized states , simulating conducting domains in a totally amorphous matrix [(43)] .

A model proposed in the study of d.c conductivity [(44)] , takes into account assumption expressed by Mott et. al [(45)] . According to which when the sample is placed in an electrical field , electron hopping takes place between localized sites . The charge carriers , moving between these sites hop from a donor to an acceptor state . In that respect each dipole has a relaxation time depending on its activation energy; the latter can be essentially attributed to existence of a potential barrier W , over which the carriers must hop [(46)] . This potential barrier , as proposed by Elliott , is due to the coulombic interaction between neighouring sites forming a dipole [(47)] . The relaxation time connected with a hop being $\tau = \tau \exp(W/K_BT)$. This model combined the imaginary part of the permittivity with the circular frequency ω of the applied electric field as :

$$\varepsilon``(\omega)=(\varepsilon_o-\varepsilon_\infty)4\pi\, N\varepsilon_o k_BT/ne^2 \int_o^\infty R`^4[\omega/(1+\omega^2\tau^2)]d\tau \qquad (1\text{-}39)$$

where R`(a function of τ) is the distance between localized sites .

Assuming $\tau << 1$, the dielectric losses can be written :

$$\varepsilon``(\omega)=(\varepsilon_o-\varepsilon_\infty)\, 2\pi^2 N(ne^2/\varepsilon_o)^3\, k_BT\, \tau_{c\rho}^{m}\, W_M^{-4}\, \omega^m \qquad (1\text{-}40)$$

With $m = -4\ k_BT\ /W_M$; n is the number of electrons that hop ; N is the concentration of localized sites ; ε_o is the static dielectric constant and ε_∞ the dielectric constant at “ infinitely high ” frequencies ; W_M is the energy required to move the electron from an site to infinite .

It can be seen that the experimental study of the dielectric losses at different frequencies and temperatures of some chalcogenide glasses reveals that (48) : $\varepsilon'' = A\,\omega^m$,

Generally the total measured conductivity , at given frequency ω , composes of two components (D.C and A.C) as :

$$\sigma_{tot}(\omega)=\sigma_{d.c}+\sigma(\omega) \qquad (1\text{-}41)$$

I-9 : Dielectric Relaxation :

The basic theory of dielectric relaxation behaviour , pointed by Owen(49), begins with amacroscopic treatment of frequency dependence . This treatment rests on two essential principals, (a) the exponential approach to equilibrium . (b) the applicability of the superposition equation .

According to Debye's theory , the dispersion equation .

$$\tau\,[d\,D(t)/dt\,]+D\,(t)=\tau\,\varepsilon_o\,\varepsilon_\infty\,[\,d\,E(t)/dt\,]+\varepsilon_o\,\varepsilon_\infty\,E(t) \qquad (1\text{-}42)$$

have the solution , the complex dielectric constant ε^* is :

$$\varepsilon^*(\omega)=D(t)/\,\varepsilon_o\,E(t)=\varepsilon_\infty+(\varepsilon_s-\varepsilon_\infty)\,/\,(1+j\omega\tau) \qquad (I\text{-}43)$$

and $$\varepsilon^*=\varepsilon'-j\,\varepsilon'' \qquad (1\text{-}44)$$

$$\varepsilon'=\varepsilon_\infty+(\,\varepsilon_s-\varepsilon_\infty\,)\,/\,(\,1+\omega^2\tau^2\,) \qquad (I\text{-}45)$$

$$\varepsilon''=(\,\varepsilon_s-\varepsilon_\infty\,)\,\omega\,\tau\,/\,(\,1+\omega^2\tau^2\,) \qquad (I\text{-}46)$$

also $$\tan\delta=\varepsilon'\,/\,\varepsilon''=[(\varepsilon_s-\varepsilon_\infty)\,\omega\tau]\,/\,[(\varepsilon_s+\varepsilon_\infty)\,\omega^2\tau^2\,]$$

The frequency dependence of ε' and ε'' is illustrated as a function of $\omega\tau$, Fig.(1-15) , and these are referred to the Debye curves for dielectric dispersion .

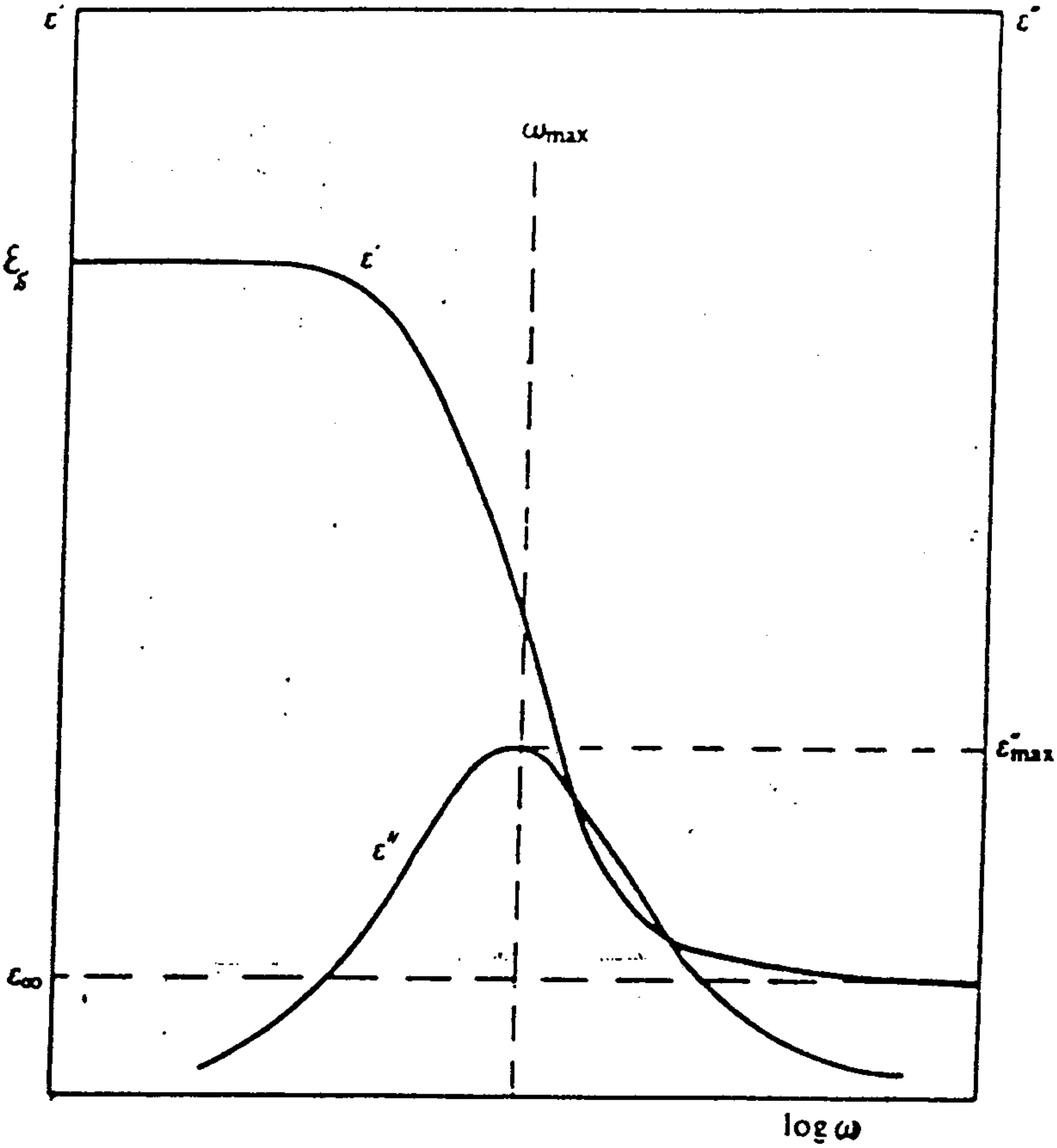

Fig (I-15) Debye dielectric dispersion curves.

The locus of equations (1-45) and (1-46) in this representation is a semicircle with its center on the real ($\varepsilon`$) axis and intercepts at ε_s and ε_∞ on this axis . This can readily be seen from eq.(1-43) which can be put in the form :

$$U + V = \varepsilon_s - \varepsilon_\infty \qquad \text{(I-47)}$$

where $U = \varepsilon^* - \varepsilon_\infty$ and $V = j\,\omega\tau\,(\varepsilon^* - \varepsilon_\infty)$

The quantities U and V considered as vectors in the complex plane are then perpendicular their vector sum being the constant real quantity (ε_s - ε_∞) . The right-angle included by these vectors is therefore inscribed in a semicircle of diameter (ε_s - ε_∞) as shown in Fig.(I-16) .

The molecular dipole orientation involves passage over a potential energy barrier with a certain probability of jumping from one orientation to another and with aid of simplifying assumptions , Kauzmann(50) obtains for the Polarization $P_{(t)}$, the electric moment per cubic centimeter , due to dipole orientation as a function of time :

$$P_{(t)} = P_o \exp(-k_o t) \qquad \text{(I-48)}$$

where P_o is the orientation Polarization at time $t = 0$ and k_o is the rate constant for the activation of dipoles , that is the jump rate made by a dipole in unit time . The jump rate k_o is related to the probability ω that a dipole molecule will move from an orientation θ , ϕ into a new position $\theta`$ , $\phi`$ within a solid angle $d\Omega$ in an interval dt by the relation .

$$\omega\,(\theta,\phi \rightarrow \theta`,\phi`) = (1/4\pi)\,k_o(\theta,\phi \rightarrow \theta`,\phi`)\,dt\,d\Omega \qquad \text{(1-49)}$$

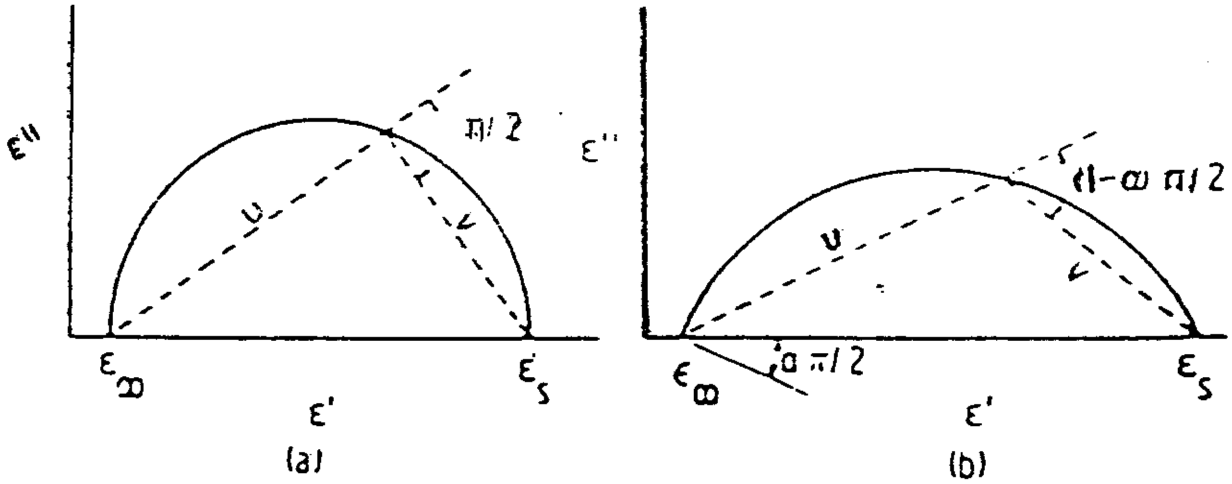

Fig.(I−16): Cole − Cole circular arc loci, ε'' vs. ε' (a) For a single relaxation time. (b) For a distribution of relaxation time

In the absence of an external field , k_o is supposed to be independent of θ and ϕ of the nature of the jump . It can then be shown that k_o is the inverse of the molecular relaxation time τ . When an external field is applied and assuming that the average time between two collisions of a particle is short compared with the period of the alternating field , then :

$$k_o = (k_B T/h) \exp(-\Delta F/RT) \qquad \text{(I-50)}$$

where ΔF is the free energy for dipole relaxation , Thus :

$$\tau = (h / k_B T) \exp(\Delta F / RT) \qquad \text{(I-51)}$$

substituting $\Delta F = \Delta H - T\,\Delta s$, equ. (I-51) may be written :

$$\tau = (h/ k_B T) \exp(\Delta H /RT) \exp(-\Delta s /R)$$

where ΔH is the heat of activation for dipole relaxation and Δs id the entropy of activation .

I-10 : Complex Impedance Method :

The principle of the impedance analysis method is based on then analysis measurement of the sample impedance taken over a wide range of frequencies and then analyzed is the complex impedance plane . Results of the measurements can be used for determining an appropriate equivalent circuit parameters(51) .

The idea , how the bulk conductivity of a sample can be estimated from the impedance analysis , will be described considering complex impedance diagram for various equivalent circuits of the sample .

First , consider a parallel combination of the RC circuit as shown in Fig.(1-17) . The impedance of such circuit at frequency ω consists of the real part R and the imaginary part ($1/\omega c$) and is written as :

$$1/Z = (1/R) + j\,\omega\, c \qquad \text{(I-52)}$$

The value z can put in the form :

$$Z = R\,(1 - j\,\omega\,\tau)\,/\,(1 + \omega^2\tau^2), \quad \tau = RC \qquad \text{(I-53)}$$

Which can be separated into the real part Z and the imaginary Z as:

$$Z = R\,\omega\,\tau\,/\,(1 + \omega^2\tau^2) \qquad \text{(I-54)}$$

$$Z = -R\,/\,(1 + \omega^2\tau^2) \qquad \text{(I-55)}$$

By elliminating $\omega\tau$ these two equations can be combined and written in the form of a circle .

$$Z^2 - Z\,R + Z^2 = 0 \qquad \text{(I-56)}$$

Adding $\frac{1}{4}R^2$ to both sides of equation , we obtain :

$$(Z' - \tfrac{1}{2}R)^2 + Z''^2 = (\tfrac{1}{2}R)^2 \qquad \text{(I-57)}$$

comparing this equation with the standard form of the equation of a circle , one can see that the Z-plane plot is a semicircle in the first quadrant with center at (½ R , O) and with a radius (½ R), Fig.(1-17) . It can be shown also that at the maximum of the semicircle $\omega\tau = 1$ where $\tau = RC$ is the time constant or the relaxation time of the circuit .

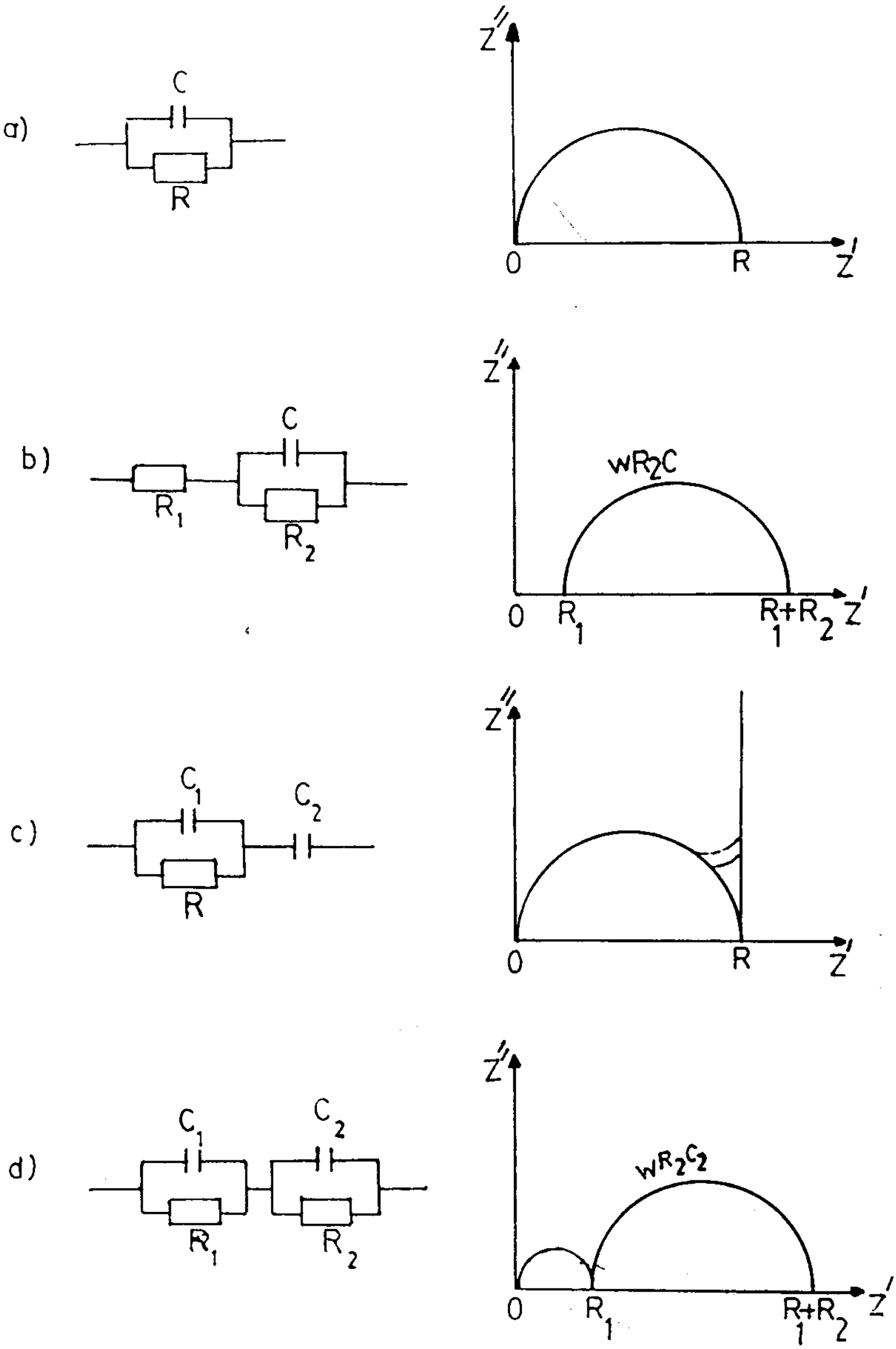

Fig.(I−17): Complex imedpance plot Z for some simple circuits RC of different combinations.

So , when from the complex impedance measurements one obtain in the complex impedance plane only one semicircle and this semicircle originates in the (0 , 0) point , it means that only one resistance R and one capacity C , both parallel combined , can be described to the sample .

In real cases it is of course not possible that a sample possesses only the bulk resistance and capacity . These parameters are most frequency combined with other parameters such as , resistance and capacity of bulk material electrode contact . In Fig. (1-17) various combinations of equivalent circuits and – corresponding impedance diagrams are presented . When the parallel R_2 C circuit is connected in series with a resistance R_1 , Fig(b) the semicircle on the complex Z plan is shifted a long Z axis . The circuit parameters can be estimated as shown in Fig. (b) . The series combination of a capacity C_1 and a parallel RC_2 circuit and its impedance diagram is shown in Fig.(c) . The most interesting is the possibility shown in Fig.(a) , i.e. series connection of two parallel circuits R_1C_1 and R_2C_2 . choosing

$$C_1 << C_2 \qquad R_2 >> R_1$$

The two semicircles in the complex impedance diagrams are well separated and all parameters can be easy estimated . The physical significance of this choice of parameters is , that region 1 , (semicircle which originates in (0,0) point) corresponds to the relatively high conducting volume of the sample and region 2 represents a highly capacitate but weakly conducting barrier . This is exactly situation which can be expected to occur in high ionic conducting bulk material physically connected with electrodes layer.

Thus , when from impedance measurement picture we obtain similar to the diagram shown in Fig.(d) , the bulk conductivity of the sample can be estimated from resistance R_1 . It is of course clear , that from such measurement it can not be decided wether this conductivity has a ionic or electronic nature .

I-11 : LITERATURE REVIEW :

The electrical conduction in oxide glasses containing transition metal ions is two different oxidation states takes place by means of small Polaron hopping (52) due to the transfer of the electrons between those different oxidation states and since the vanadium exists a mainly in our system in the velency states V^{5+} and V^{4+} , therefor the conduction process in the glasses may be attributed to the hopping of 3d – electrons from the V^{4+} to V^{5+} ions , the activation energy of this hopping process is equal to 0.32 eV at low temperatures.

LINSIEY , et al (53) have been prepared V_2O_5–P_2O_5 glasses in different molar ratio of 90 , 80 , 70 , 60 and 50 mole % V_2O_5 with 10, 20 , 30 , 40 and 50 mole % P_2O_5 . The mixture melted for 30 min . at 700 – 800 °c , and annealing at 270 – 300 °C for 2 hr . They have measured d.c conductivity as well as a.c conductivity as a function of the ratio V^{4+}/V_{total} d.c conductivity has been measured over a wide range of temperature for one samples from each of the four systems with 90 , 80 , 70 and 60 mole % V_2O_5 . The polts of logσ versus 1/T are approximately linear high temperature ($\geq$ 225 °c) but clearly become increasingly non linear as the temperature is reduced . The activation energy has been calculated form the tangent of these curves , and found to be greater in the sample 90 mole % V_2O_5 . They also found that the activation energy changes as the ratio V^{4+}/V_{total} is varies .

The minimum value of the activation energy and also a tendency for E to increase as the amount of total vanadium is decreased .

KASHIF et al (54) were studied the effect of heat treatment time on the electrical conductivity of the vanadium phosphate glass system. Powders of pure chemicals were mixed thoroughly and the resulting homogenous mixture was melted at 800 °C for 2 hr . The glass was quenched in air and annealed at 200 °C for 2 hr . To prepare a 84 mole % V_2O_5 – 16 mole % P_2O_5 glass sample . The glass obtained was heat treated at 350 °C for 30, 60 , 90 and 120 min. The electrical conductivity depend on the fact that the vanadium is present in different valency states and it is accupied that these material are electronic conductors in which the transport meachanism involves the exchange of electron between V^{4+} and V^{5+} ions . A maximum was observed in conductivity measurements when the ratio V^{4+}/V^{5+} was equal to one . They also found that the conductivity of the heat – treatment time . This behaviour could result from the variation in the microstructure of the samples due to the heat – treatment .

KUTUB . et al (55) studied the dependence of electrical conductivity of vanadium phosphate glasses on the relative concentration of V^{4+} and V^{5+} ions . It is found that the addition of CuO, which acts as an oxidizing agent . alters the ratio of concentration of vanadium ions . Thus the conductivity is decreased with increasing the CuO content . The conductivity measurement have revealed on electron conduction phenomenon in the glasses .

GHOSH , et al (56) have studied the ternary vanadium glasses of composition 50 V_2O_5 – (50 – x) P_2O_5 – X M_2O_3 with M = B1 and Sb which have been prepared by rapidly quenching . The d.c conductivity of the annealed glass have been measured and Mott's Polaron theory has been applied to explain the thermal variation of the conductivity data . The conductivity of vanadium phosphate containing $Bi_2 O_3$ are always found to be higher than that of the base glass (50 V_2O_5 – 50 P_2O_5) .

The conductivity of glasses containing $Sb_2 O_3$ are always lower than that of the base glass . The activation energy in case of $Bi_2 O_3$ was found to depend on the compositions , while in case of $Sb_2 O_3$ are not .

CALESTANI et al (57) have been prepared V_2O_5 – Zn O glass taking 50 , 60 , 66.7 , 71.4 and 75 mole % V_2O_5 with 50 , 40 , 33.3 , 28 .6 and 25 ZnO , the mixture melted at 750 °C for 3 hr . The samples were annealed at 120 °C for 2 hr , and the d.c conductivity was measured . The value of the pre-exponential parameter , A , and the activation energy , w can calculated using the formula $\sigma = A \exp(-w/k_BT)$. The value of A and w smoothly increase and decrease as a function of the molar V_2O_5 percentage in the composition . The factor A can give information about the nature of the conduction mechanism .

KHAN , et al (58) prepared systems having the composition expressed in mole % 50 P_2O_5 – (50 – x) V_2O_5 , where x is kept at 5 mole % from rare – earth oxides , $(RE)_2 O_3$. D.C conductivity of the samples annealed at 300 °C and 500 °C) was measured . The conductivity of V_2O_5 – P_2O_5 is slightly higher than the corresponding compositions with rare – earth oxides . The heat treatment caused progressive microstructural changes with affected the electronic conductivity and the activation energy for conduction .

MANINGH , et al [(59)] have measured the d.c conductivity and dielectric properties of glasses of composition (70 – x) V_2O_5 , x Mo O_3 , 30 P_2O_5 as a function of temperature and frequency for $0 < x < 5$ mole % . An increase in conductivity by two orders of magnitude is observed for 1 mole % Mo O_3 and this is correlated with changes in activation energy . The result can be explained in terms of small Polaron theory with the main interaction being through the local electronic Polarizability at any site . The results indicate that percolatoin considerations have to be taken into account in describing the electrical properties of transition metal glasses .

HIRASHIMA , et al [(60)] have prepared $V_2O_5 - TeO_2$ glasses in a different moler fraction 55 , 50 and 40 V_2O_5 with 45 , 50 and 60 mole % TeO_2 . The mixture melted at 800 °C and annealed at 150 °C for 4 hr . d.c electric field up to about 10^6 V/cm was applied to $V_2O_5 - TeO_2$ glass film of 2 – 20 μm in thickness , and memory switching was observed . The conductivity increased two orders of magnitude or more crystallization of these glasses by heat treatment also caused to increase in conductivity of similar magnitude .

The threshold field of switching depend on the temperature but not on the film thickness L , for $L \leq 5$ mm . The dependence of the delay time on the applied field and film thickness were deviated from those predicated from electrothermal switching theory for $L \leq 5$ μm . Or applied field $\leq 10^5$ V/cm .

It was discussed that in these regions the electronic switching mechanism could be applied.

MANTANI, et al (61) have measured the electrical behaviour of 0.4 TeO_2 – 0.6 V_2O_5 glasses samples by current – voltage dependence with constant current. The results show increasing deviation from the Ohm's law with increasing current density leading to a maximum voltage at large current densities. This electrical behaviour, described in a literature as a switching phenomenon is interpreted assuming that the Joul effect resulting from the current passing through induces large increases of the glass conductivities.

The dependence of the dielectric properties of transition metal ions glasses of temperatures as well as the frequency have been studied by many authors. Conductivity and dielectric properties of semiconducting glasses of composition 80 % V_2O_5, 20 % P_2O_5 have been measured as a function of frequency from d.c to 3.6 GHz over a temperature range from 77 to 420 K, a first of the results to a model of Polaronic hopping conduction leads to an activation energy due to disorder $\Delta w = 0.09$ eV at 77 K and an optical phonon energy to 0.053 eV compared to a calculated Miller Abrahams energy of approximately 0.12 eV. The real and imaginary parts of the a.c conductivity are shown to increase the frequency according to power law $\sigma = A\omega^s$, where s = 0.83 to 0.95..

The results are shown to be consistent with a model of a.c conduction normally applied to impurity – doped broad band semiconductors, and differences between the temperature dependence of the d.c and a.c conductivity are attributed to a distribution of site energy of the glass .

ASWINI CHOSH [(62)] measured the frequency – dependent (a.c) conductivity (real as well as imaginary parts) for various compositions of the bismuth – vanadium glassy semi-conductors in the frequency range $10^2 - 10^5$ Hz and in the temperature range 77 – 420 K . The behaviour of the a.c conductivity is Bradley similar to what has been observed previously in many other types of amorphous semi-conductors , namely , nearly linear frequency dependence and weak temperature dependence , their experimental results are analyzed with reference to various theoretical models based on quantum – mechanical tunneling and classical hopping over barriers . The analysis shows that the temperature dependence of the a.c conductivity is consistent with the simple quantum – mechanical tunneling model at low temperature .

The correlated barrier hopping model is consisted with the temperature dependence of both the a.c conductivity and it is frequency exponent .

ASWINI GHOSH [(63)] measured d.c as well as frequency dependent (real imaginary parts) for various compositions of the vanadium germanate glassy semi conductors in the temperature range 80–420 K .

The experimental results are analyzed with reference to various theoretical models proposed for electrical conduction in amorphous semi-conductors . The analysis showed that at higher temperature the temperature dependence of the d.c conductivity is consistent with Mott's model of polaron – assisted polaronic hopping conduction in the adiabatic approximation . The temperature dependence of a.c conductivity is consistent with the simple quantum – mechanical tunneling model at lower temperature . The overlapping large – polaron tunneling model can explain the temperature dependence of frequency exponent at low temperature however , this model predicts a temperature dependence of the a.c conductivity much higher than the observed data .

SAYER. et al (64) measured a.c conductivity and dielectric properties dependence on the frequency and temperature of phosphate glasses based on (V_2O_5 , Ti O_3 , Mo O_3 , Fe_2 O_3 , Cu O , SiO , NiO , CaO , Mn_2 O_3 and W O_3) . The vanadium system is examined in a range of compositions , most of others in the composition 50 mole % oxide . A polaronic model is generally applied , and the variation of activation energy for conduction with type of glass and transition metal ions spacing is found to dominate the magnitude of the conductivity . Measurement of the static dielectric constant show no effects of disorder high temperature .

MARASHI (65) studied the frequency and temperature dependence of total conductivity for V_2O_5 - P_2O_5 glass . They found that the frequency exponents decreases with increasing temperature and applied two models to explain a.c conductivity : the quantum – mechanical tunneling and classical hopping over the barrier activation energy and the redius of the polaron .

EL MANSY et al $^{(66)}$ have prepared (V_2O_5)$_{(1.x)}$(P_2O_5)$_{(x)}$ glasses (x=0.12 , 0.18 , 0,24 and 0,30) . The mixture melted for 7 hr. at 700°C . They have measured I-V Characteristics for the glass sample shows three regions of conduction , namely high resistance state , turnover point and differential negative resistance region . The turnover point is shifted towards higher voltage as the sample thickness is increased at high field conditions Polaronic conduction increase with increasing applied electric field . On the other hand the increase of scattering of charge carriers at high field results in some energy dissipation in the conduction path filament . The rise of temperature in the conduction path will enhance the conduction process as a result of increasing charge carrier concentration . This conforms that the turnover in I-V curve is an electrothermal process . The observed variation of current with applied voltage in negative – resistance region suggests field dependence of conduction which is based on charge carrier hopping between localized states .

K. NASSAU AND D.W. Murphy $^{(67)}$ studied electrochemical reaction and the quenching for the Li_2O - V_2O_5 glasses .

It has been noted that oxygen evolution during the crystallization of high V_2O_5 compositions from the melt , resulting in a crystal of lower oxygen content than the melt .

The quenched glass as well as the subsequently crystallized solid can be expected to have the same oxygen content as the melt being quenched . This explains the change in color of the quenched V_2O_5 glasses with variation of the melt temperature .

The reaction with Lithium is reversibly depend on a continuous path for Lithium diffusion such as is provided by two – dimensional layers in crystalline Li V_3 O_8 or one – dimensional channels as in crystalline V_2O_5 .

H. JAIN , C.H HSIEH (68) studied the electrical conductivity of several solids , sodium aluminosilicate (Na_2O - Al_2O_3 2.2 Si O_2) glass , a quartz crystal and lithium triborate glass . The d.c conductivity value are taken from complex impedance plots . Three frequency window are chosen to examine the effect of window on exponents in the a.c conductivity .

The important observation find from the analysis as , the frequency window increase from the low frequency side encompassing higher and higher frequency region , s decreases , note that s is most sensitive to the window width in the frequency region . The conductivity data of lithium triborate glass . Two frequency windows are chosen to analyze the data of $\sigma(\omega)$ 20 Hz to 100 Hz . It gives s = 0.66 . The other is from 20 Hz to 5 kHz . It gives s = 0.75 .

B. WANG et al (69) discuss the effect of nitrogen on the structure and ionic conductivity of bulk lithium phosphours oxynitride glasses. The ionic conductivity σ of the glasses calculate from the impedance data , plots of σ T vs 1/T for the lithium metaphosphate oxynitride glasses . Two conduction processes of two phase steps in Re (Z) , due to the presence of two phases with different conductivites .

The existence of two conduction phases in the lithium metaphosphate oxynitride glasses in apparently caused by the nitridation . The increase of conductivity due to the decrease in activation energy after nitridation .

The higher ionic conductivity in the higher lithium content caused by a decrease in activation energy on nitridation . The increase of ionic conductivity can be attributed to the structural changes as the result of nitrogen incorporation into the glass , and the decreasing electrostatic energy after nitridation .

M. HORIUCHI (70) studied mixed glasses containing lithim chloride and amphoteric oxide with compositions $x (z LiCl) - y (Li_2O) . (100 - x - y) P_2O_5$ and $x Al_2O_3 - y (2 LiCl) . (100 - x - y) P_2O_5$. The d.c conductivity measured the time dependence of conductivity under constant d.c voltage , found that the result suggest that the ions transport > 99.9 % of the electronic current in the glass .

The ion , electron transport ratio was > 99 % , these means that these glasses are pure ionic conductors . The temperature dependence of the conductivity was measured , the conductivity increases with increasing lithium chloride content , and the activation energy decreases with increasing lithium chloride . Conductivity of the glass containing Al_2O_3 is higher than the glass containing lithium chloride. The addition of Li Cl in both systems destroys the P – O – P glass network by Cl ions and the resulting open structure is favorable to the migration of Li^+ ions .

DURAN et al [71] studied the electrical and dielectric properties of the $P_2O_5 - BaO - CuO$ glass system. The time dependence of d.c conductivity indicates that conduction is mainly electronic character of these glasses. The linear behavior of log I against $V^{1/2}$ during the preswitching process implies a thermal ionic or electronic mechanism. The temperature and frequency dependence of the loss tangent and dielectric constant is explained by a Debye dielectric relaxation process with a relaxation time distribution. The activation energies of this process conicide with obtained in a d.c region, suggesting that the conduction mechanism in the same in both regions.

The frequency dependence of total conductivity fits the equation $\sigma \alpha \omega^n$, n being a function of ratio Cu^+ / Cu_{tot}. For low Cu^+ contents n is agrees with the theoretical predications for phonon activated conduction mechanisms. The values obtained for higher copper concentrations may be explained by the appearance of delocalized states.

El MANSY [72] studied the electrical conduction and dielectric relaxation in $(V_2O_5)_{1-x} - (P_2O_5)_x$ glasses where : x = 0.12, 0.18 and 0.24 in the temperature range 300 – 560 K and frequency range 50 Hz – 10 Hz. The temperature dependence of bulk conductivity are obtained and show on increase with increasing V_2O_5/P_2O_5 ratio and also increase with increasing temperature.

The value of activation energies lie in the range 0.0355 – 0.0546 eV. The d.c conductivity shows on activated with increasing temperature, the activation energy decreases with increasing V_2O_5.

Our estimation shows that the polaron bandwidth , satisfies the conduction for adiabatic hopping of small polarons . The frequency dependence of the total conductivity was studied , the polaron model is generally applicable with evidence that hopping occurs . The value of n lies in the range 0.65 - 1.09 .

ABHA , MANSINGH , et al (73) studied the dielectric behaviour V_2O_5 , T_2O_5 glasses were prepared from 10 mole% 80 mole % V_2O_5.

The sample annealed at 150 °C for 3 hr . Data of a.c conductivity and dielectric constant with temperature and frequency have been analyzed in terms of conventional dipolar dielectric relaxation using dielectric models .

The glass former TeO_2 gives rise of the value of dielectric constant then the analogous phosphate glasses .

EL - MANSY (74) , studied the pressure and temperature effect on the I-V Characteristics curves in Ge_{27} Te_{62} Se_{11} chalcogenide glasses in the temperature range 301 – 359 K and pressure range up to 7.15×10^4 pas . The general behaviour is shifted towards lower voltage and higher current when the ambient temperature and the applied pressure were increased . The effect of pressure on the non-linear conduction can be analyzed on the basis of Pool-Frankel effect in the prebreak-down region , emission of electrons from filled to empty sites located at a distance in the range 4.5 – 36 Å .

The application of pressure showed a pronounced effect on the topology of the band structure which reduces the energy gap width .

The effect of applied field essists the emission of electron from deep traps at a depth of 0.372 eV below the conduction band , joule heating in the conduction path under the infiucnce of high field initiates the onest of breakdown and subsequently the differential negative resistance .

The voltage dependence of the negative resistance showed the possibility of electron hopping between filled and empty localized states located at distance in the range of (92 – 206 $\overset{o}{A}$) . The density of localized states is estimated which lies in the range 5.7 x 10^{16} – 1.8x 10^{18} Cm^{-3} /eV .

El - MANSY et al (75) studied the pressure effect on turnover behaviour in I-V Characteristic curves in chalcogenide glasses , they found that the turnover point is shifted towards lower voltage and higher current when the applied voltage was increased . They attributed their results to the orientation of dipoles randomly dispresed in viscous amorphous matrix .

I-12 : Aim Of The Work

Vanadium phosphate glasses are very important in applications as semiconducting materials . These glasses are promising because of their application as positive electrodes in high-efficiency solid electrochemical cells, microbatteries , sensors smart windows , and as switching devices in the electronic circuits .

The previous studies showed that the electrical conduction of the vanadium phosphate glasses can be greatly controlled by varying the reduction / oxidation ratio of the transition metal (vanadium) and/or by increasing the vanadium fractional in the glasses . However, the present work aims to study the influence of the addition of lithium phosphate in order to reduce the vanadium (V^{5+} to V^{4+}) and its reflection on the electrical conduction and dielectric properties of the glasses .